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**Mathematics.** — “*Ueber das Komitantensystem zweier und dreier ternärer quadratischer Formen*”. By B. L. VAN DER WAERDEN.  
(Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of February 24, 1923).

Ein volles Komitantensystem für zwei ternäre quadratische Formen (“Kegelschnitte”) ist aufgestellt worden von GORDAN, und findet sich bei CLEBSCH <sup>1)</sup>. Ein solches für 3 Kegelschnitte ist unabhängig voneinander von CIAMBERLINI <sup>2)</sup>, von BAKER <sup>3)</sup> und von FISCHER und MUMMELTER <sup>4)</sup> aufgestellt worden. Das CIAMBERLINI’sche System besteht, wenn man die “identische” Komitante  $u_x$  hinzurechnet, aus 128 Formen, das BAKER’sche aus 148, das FISCHER—MUMMELTER’sche aus 185 Formen. In der Tat sind 20 von den BAKER’schen Formen mittels der CIAMBERLINI’schen Formen reduzibel (siehe § 2), während SEELIG <sup>5)</sup> gezeigt hat, wie sich die FISCHER—MUMMELTER’schen Formen auf die CIAMBERLINI’schen reduzieren. Schliesslich rührt ein vollständiges Typensystem für eine unbeschränkte Anzahl Kegelschnitte (oder, was auf dasselbe hinauskommt, für 5 Kegelschnitte) her von TURNBULL <sup>6)</sup>, der daraus ein vollständiges Formensystem für 4 Kegelschnitte ableitet, bestehend aus 784 Komitanten.

Mein *Zweck* ist, zu zeigen:

- in § 1, dass die 21 Formen von GORDAN irreduzibel sind,
- in § 2, dass von den 128 CIAMBERLINI’schen Formen 6 reduzibel sind,
- in § 3, dass die übrigen 122 irreduzibel sind.

Die *Methode* der Irreduzibilitätsbeweise beruht auf dem folgenden evidenten Prinzip: Soll eine Reduktionsformel für eine Komitante gelten, so muss sie auch dann noch gelten, wenn man die Urformen spezialisiert, z.B. sie miteinander identifiziert, oder auch statt der symbolischen Quadrate  $\alpha_x^2$  wirkliche Quadrate  $v_x^2$  einführt. Ich werde dementsprechend in den §§ 1 und 3 alle apriori möglichen homogenen Reduktionsformeln für die betreffenden Kom-

<sup>1)</sup> CLEBSCH-LINDEMANN, Vorlesungen I, Abt. III § VIII, p. 291 (Leipzig 1876)

<sup>2)</sup> Giornale di Battaglini 24 (1886) p. 141.

<sup>3)</sup> Trans. Camb. Phil. Soc., Vol. 15, Part I (1894) p. 62.

<sup>4)</sup> Monatshefte für Mathematik und Physik 8 (1897), p. 97.

<sup>5)</sup> " " " " " 29 (1918), p. 225.

<sup>6)</sup> Proc. London Math. Soc. (2) 9 (1910) p. 81.



tanten (mit unbestimmten Koeffizienten) aufstellen und sodann, durch verschiedene Spezialisierungen und nachfolgende geometrische Betrachtungen, deren Unmöglichkeit zeigen.

Die ersten Ansätze zu Irreduzibilitätsbeweisen finden sich bei TURNBULL<sup>1)</sup> er zeigt auf Grund der Identifizierung, dass gewisse Komitanten für 4 Kegelschnitte irreduzibel sind, vorausgesetzt dass gewisse Komitanten für 3 Kegelschnitte es sind. TURNBULL fügt hinzu, er sehe noch nicht ein, wie man sonst noch Irreduzibilitätsbeweise geben könnte.

Die *Bezeichnungen* schliessen sich an CLEBSCH und CIAMBERLINI an, obzwar später bessere Methoden eingeführt worden sind. Die Urformen heissen

$$\begin{aligned} f_1 &= a_x^2 = b_x^2 = \dots \\ f_2 &= a'_x{}^2 = b'_x{}^2 = \dots \\ f_3 &= a''_x{}^2 = b''_x{}^2 = \dots \end{aligned}$$

Die Kontravarianten der einzelnen Urformen werden bezeichnet als

$$\begin{aligned} F_{11} &= (a b u)^2 = u_\alpha^2 = u_\beta^2 = \dots \\ F_{22} &= \text{u.s.w.} \end{aligned}$$

Von BAKER übernehme ich noch die folgenden Abkürzungen:

$$u = \overline{xy} \text{ bedeutet } u_1 = x_2 y_3 - x_3 y_2, \text{ u.s.w.}$$

$$(vw \cdot xy) = (\overline{vw} \cdot \overline{xy}) = (v w \overline{xy}) = v_x w_y - v_y w_x.$$

$\overset{r}{A} = 0$  bedeutet:  $A$  ist reduzibel zu einfacheren Formen (d. h. Formen deren Gesamtgrad in allen Koeffizienten und Variablen niedriger ist).

$\overset{r}{A} = B$  bedeutet:  $A = B +$  reduzibele Glieder (bei BAKER  $\equiv$ ).

$=$  oder  $\equiv$  bedeutet: identisch gleich für alle Werte der  $u, x, a_{ik}, a'_{ik}, a''_{ik}$ .

Ich werde die folgenden *Reduktions-Identitäten* verwenden<sup>2)</sup>:

$$(a) \quad a_\alpha a_y v_\alpha = \frac{1}{3} a_\alpha^2 \cdot v_y \quad \overset{r}{=} 0$$

$$(b) \quad (abv) a_y b_z = \frac{1}{2} v_\alpha (ayz) \quad \overset{r}{=} \frac{1}{2} v_\alpha (ayz)$$

$$\text{dual: } (c) \quad (\alpha\beta\gamma) v_\alpha w_\beta = \frac{2}{3} a_\alpha^2 \cdot b_\gamma (bvw) \quad \overset{r}{=} 0$$

$$(d) \quad a_\gamma b_\gamma a_y b_z = a_\gamma^2 \cdot b_\gamma b_z - \frac{1}{2} (a\varphi\gamma) (a\varphi z) \quad \overset{r}{=} -\frac{1}{2} (a\varphi\gamma) (a\varphi z)$$

$$\text{dual: } (e) \quad g_\alpha g_\beta v_\alpha w_\beta = g_\alpha^2 \cdot v_\beta w_\beta - \frac{2}{3} a_\alpha^2 \cdot (bgv) (bgw) \quad \overset{r}{=} 0$$

<sup>1)</sup> Proc. London Math. Soc. (2) 9 (1910), p. 120.

<sup>2)</sup> CLEBSCH—LINDEMANN, I, III, § VIII. Am übersichtlichsten findet man die Identitäten, sowie die Ableitung des Formensystems zweier Kegelschnitte, bei GRACE and YOUNG, Algebra of Invariants, § 228.

$$(f) \ a_p b_q a_r b_s = a_p b_q a_r b_s + \frac{1}{2} (apq)(ars) \stackrel{r}{=} a_p b_q a_r b_s + \frac{1}{2} (apq)(ars)$$

$$\text{dual: (g) } p_\alpha q_\beta r_\gamma s_\delta = q_\beta p_\gamma r_\alpha s_\delta + \frac{2}{3} a_\alpha^2 \cdot (apq)(ars) \stackrel{r}{=} q_\beta p_\gamma r_\alpha s_\delta$$

wo  $\varphi, g, y, z, v, w, p, q, r, s$  beliebige Symbole sind.

Dazu kommen die fundamentalen Identitäten des ternären Gebietes.

*Bemerkung.* Man kann von einer jeden Identität zu der dualistisch entsprechenden übergehen, indem man jedes  $a$  durch  $a$ , jedes  $a'$  durch  $a'$ , usw., jedes  $x$  durch  $u$ , und umgekehrt, ersetzt, und sodann, wo nötig, durch Hinzufügung von Faktoren  $\frac{4}{3} a_\alpha^2, \frac{4}{3} a_{\alpha'}^2$ , usw., die erhaltene Formel homogen macht. Denn wenn man  $a$  durch  $a$  ersetzt, so müsste man eigentlich  $a$  ersetzen durch  $\bar{a}$ , definiert durch  $\bar{a}_x^2 = (a\beta x)^2$ ; es ist aber  $(a\beta x)^2 = \frac{4}{3} a_\alpha^2 \cdot a_x^2$ .

### § 1. Irreduzibilität des Systems für zwei Kegelschnitte.

Ich werde das GORDANSche System hinschreiben, dabei aber von je zwei Formen, die durch Vertauschung der beiden Kegelschnitte in einander übergehen, nur eine behalten. In Klammern füge ich hinzu die 4 Grade der Komitanten in  $a_{ik}, a'_{ik}; u, v$ . Eine danebenstehende Zahl bezeichnet die Anzahl der analogen Formen. Dualistisch gegenüberstehende Formen sind mit den entsprechenden Griechischen und Lateinischen Buchstaben benannt, oder auch durch obere Querstriche unterschieden.

$u_x$	(00.11)	1	$N_{1,2} = (a a' u) a_x a'_x$	(11.12)	1
$f_1 = a_x$	(10.02)	2	$C_{1,2} = (a a' u) a'_\alpha a_\alpha u_\alpha$	(31.21)	2
$F_{11} = u_\alpha^2$	(20.20)	2	$\bar{N}_{1,2} = (\alpha a' x) u_\alpha u_{\alpha'}$	(22.21)	1
$F_{1,2} = (a a' u)^2$	(11.20)	1	$\Gamma_{1,2} = (\alpha a' x) a_{\alpha'} u_\alpha a_x$	(32.12)	2
$A_{111} = a_\alpha^2$	(30.00)	2	$D_{1,2} = (a a' u) a_{\alpha'} a'_\alpha u_\alpha u_{\alpha'}$	(33.30)	1
$A_{112} = a'_{\alpha'}^2$	(21.00)	2	$\Delta_{1,2} = (\alpha a' x) a_{\alpha'} a'_\alpha a_x a'_x$	(33.03)	1
$B_{1,2} = a'_\alpha a'_x u_\alpha$	(21.11)	2			
$\Phi_{1,2} = (a a' x)^2$	(22.02)	1			

Die apriori möglichen homogenen Reduktionsformeln sind:

$$\begin{array}{ll}
 (1) \ F_{11} = 0 & (7) \ N_{1,2} = 0 \\
 (2) \ F_{1,2} = 0 & (8) \ C_{1,2} = 0 \\
 (3) \ A_{111} = 0 & (9) \ \bar{N}_{1,2} = 0 \\
 (4) \ A_{112} = 0 & (10) \ \Gamma_{1,2} = \lambda \cdot A_{112} \cdot N_{1,2} \\
 (5) \ B_{1,2} = \lambda \cdot A_{112} \cdot u_x & (11) \ \quad = 0 \\
 (6) \ \Phi_{1,2} = \lambda A_{112} f_1 + \mu A_{122} f_1 & (12) \ \Delta_{1,2} = 0
 \end{array}$$

Jetzt gehe ich daran, die Unmöglichkeit jeder dieser Formeln zu beweisen:



- (1) Aus der Geometrie des Kegelschnittes weiss man, dass (1)  
 (3) und (3) nicht gelten.  
 (2) (1) und (3) sind aber Spezialisierungen von (2) en (4). Daher  
 (4) können auch diese nicht gelten.  
 (5)  $B_{1,2} = 0$  stellt, bei variablem  $x$ , die Gleichung der Polare  $^{\circ}$  des  
 Pols  $'$  von  $u$  dar (Pol  $^{\circ}$  bedeutet: Pol bezüglich  $f_1$ , Pol  $'$   
 bedeutet: Pol bezüglich  $f_2$ ).  $B_{1,2}$  ist somit nicht identisch Null.  
 • Auch fällt diese Polare nicht für jedes  $u$  mit  $u$  selbst zusammen,  
 es sei denn, dass die beiden Polarsystemen identisch seien;  
 $B_{1,2}$  enthält also nicht allgemein den Faktor  $u_x$ : (5) gilt nicht.  
 (6) In (6) spezialisire man  $a_x^2 = v_x^2$ . Jede Form, welche ein  
 Symbol  $a$  enthält, verschwindet dann. Das ergibt  $\Phi_{1,2} = 0$ ,  
 $A_{1,12} = 0$ ,  $A_{1,2} \neq 0$ ,  $f_1 \neq 0$ , und daher  $\mu = 0$ . Ebenso beweist  
 man  $\lambda = 0$ . Aus (6) wird  $\Phi_{1,2} = 0$ . Die dazu duale Formel (2)  
 gilt aber nicht, daher kann auch (6) nicht gelten.  
 (7) Die beiden Polaren des Punktes  $x$  seien:

$$v = a \cdot a_x \quad ; \quad w = a' \cdot a'_x.$$

Sie sind im Allgemeinen weder unbestimmt, noch miteinander  
 identisch. Daher ist  $N = (v w u) \equiv \neq 0$ , oder (7) gilt nicht.

- (9) Die dualistische Betrachtung gilt für (9).  
 (8) Die Polare  $'$  des Pols  $^{\circ}$  von  $u$  sei

$$v = a' \cdot a'_\alpha u_\alpha.$$

Weiter sei  $\overline{uv} = y$ . Da  $v$  nicht mit  $u$  zusammenfällt (siehe  
 unter (5)), so ist  $y$  nicht unbestimmt. Nun ist  $C_{1,2} = a_x a_y \equiv \neq 0$ ,  
 oder (8) gilt nicht. Die dualistische Betrachtung ergibt, dass  
 in (10)  $\lambda \neq 0$  sein muss.

- (10) In (10) setze man  $a'_x^2 = v_x^2$ . Jede Form, welche ein Symbol  
 $a'$  enthält, verschwindet dann, und es wird  $\Gamma_{1,2} = 0$ ,  $N_{1,2} \neq 0$ ,  
 $A_{1,12} \neq 0$ , und daher  $\lambda = 0$ , in Widerspruch mit dem Vorher-  
 gehenden.  
 (11)  $D_{1,2}$  stellt das Produkt der linken Seiten der Gleichungen  
 der drei Seiten des den beiden Kegelschnitten gemeinsamen  
 Polardreiecks dar, und kann somit nicht identisch verschwinden  
 (12) Der dualistische Beweis gilt für  $\Delta_{1,2}$ .

## § 2. Reduktion der Formen $\overline{M}_{ik}$ und $\overline{T}_i$ von CIAMBERLINI.

Es sei

$$\overline{M}'_{2,3} = (a a'' x) a_\alpha a_{\alpha''} u_{\alpha'} u_\alpha \quad ; \quad \overline{M}'_{3,2} = (a a' x) a_{\alpha'} a_{\alpha''} u_\alpha u_{\alpha'}.$$

CIAMBERLINI hat bewiesen<sup>1)</sup>

<sup>1)</sup> Giornale di Battaglini, 24, p. 150, a.





$\frac{1}{2} a_{x'} u_{x'} (a'' a' a) a_x u_x - \frac{1}{2} a_{x'} u_{x''} (a'' a' a) a_x u_x - \frac{1}{2} a_{x''} u_x (a'' a' a) a_x u_{x'} \stackrel{r}{=} 0$   
 oder, da das erste und dritte Glied einander gleich sind,

$$(a a'' a') a_x a_{x''} u_{x'} u_x + \frac{1}{2} (a a' a'') a_x a_{x'} u_{x''} u_x \stackrel{r}{=} 0 \quad . \quad . \quad . \quad (5)$$

Aus (2), (3), (5) folgt:

$$\bar{M}'_{2,3} + \frac{1}{2} \bar{M}'_{3,2} \stackrel{r}{=} 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Endlich folgt aus (1) und (6):

$$\bar{M}'_{2,3} \stackrel{r}{=} \quad ; \quad \bar{M}'_{3,2} \stackrel{r}{=} 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

und somit: die drei CIAMBERLINI'schen Formen

$$\bar{M}_{23} = \bar{M}'_{2,3} + \bar{M}'_{3,2} \quad ; \quad \bar{M}_{31} = \bar{M}'_{3,1} + \bar{M}'_{1,3} \quad ; \quad \bar{M}_{12} = \bar{M}'_{1,2} + \bar{M}'_{2,1}$$

sind reduzibel.

Der andere reduzibele Typus des CIAMBERLINI'schen Systems ist:

$$\bar{T}_1 = (a a' a'') (a a'' x) (\beta a' x) u_\beta .$$

Nach (e) ist in einer Komitante jedes  $\alpha$  mit jedem  $\beta$  vertauschbar, daher:

$$(a a'' u) a'_\beta a''_\alpha b'_\beta b''_\alpha b'_x b''_x \stackrel{r}{=} (a' a'' u) a'_\alpha a''_\alpha . b'_\beta b''_\beta b'_x b''_x \stackrel{r}{=} 0$$

Auf der linken Seite wenden wir (d) an auf die Faktoren  $a'_\beta b'_\beta$

$$(a' \beta . a'' u) (a' \beta x) a''_\alpha b''_\alpha b''_x \stackrel{r}{=} 0$$

$$a''_\alpha u_\beta (a' \beta x) a''_\alpha b''_\alpha b''_x - a''_\beta u_{x'} (a' \beta x) a''_\alpha b''_\alpha b''_x \stackrel{r}{=} 0 .$$

Im zweiten Gliede dieses Ausdruckes ergibt abermalige Vertauschung eines  $\alpha$  mit einem  $\beta$  einen wirklichen Faktor  $a''_\alpha{}^2$ . Folglich ist das zweite Glied zu vernachlässigen. Auf das erste Glied wenden wir wiederum (d) an, jetzt auf die Faktoren  $a''_\alpha b''_\alpha$  und finden

$$(a'' a a') (a'' a x) u_\beta (a' \beta x) \stackrel{r}{=} 0$$

oder

$$\bar{T}_1 \stackrel{r}{=} 0 .$$

Ebenso

$$\bar{T}_2 \stackrel{r}{=} 0 \quad ; \quad \bar{T}_3 \stackrel{r}{=} 0 .$$

### § 3. Irreduzibilität des Systems für drei Kegelschnitte.

Mit Weglassung der Formen die nur von zwei der drei Kegelschnitte abhängen, und der reduzibelen Formen  $\bar{M}$  und  $\bar{T}$ , besteht das CIAMBERLINI'sche volle System für drei Kegelschnitte aus den folgenden Formen:

$L$	$= (a' a'' a'')^2$	(111.00)	1
$V_1$	$= (a' a' a'') (a' a'' u) a_x$	(111.11)	2 <sup>1)</sup>
$S_{2,3}$	$= a'_\alpha a''_\alpha a'_x a''_x$	(211.02)	3
$\Sigma_{2,1}$	$= a_{\alpha'} a_{\alpha''} u_{\alpha'} u_{\alpha''}$	(122.20)	3
$A$	$= (a' a' a'')^2$	(222.00)	1
$\bar{V}_1$	$= (a' a' a'') (a' a'' x) u_\alpha$	(222.11)	2 <sup>2)</sup>
$P_{2,3}$	$= a_{\alpha'} a_{\alpha''} a''_{\alpha'} a''_x u_{\alpha''}$	(123.11)	6 <sup>3)</sup>
$H$	$= (a' a'' u) (a'' a u) (a' a' u)$	(111.30)	1
$I$	$= (a' a' a'') a_x a'_x a''_x$	(111.03)	1
$O_1$	$= (a' a'' u) a'_\alpha a''_\alpha$	(211.10)	3
$E_{2,3}$	$= (a' a'' u) a''_\alpha u_\alpha a'_x$	(211.21)	6 <sup>4)</sup>
$T_1$	$= (a' a' a'') (a' a'' u) (b' a' u) b_x$	(211.21)	3
$X_1$	$= (a' a' a'') a_x a'_\alpha a''_\alpha$	(311.01)	3
$\Omega_1$	$= (a' a'' x) a_{\alpha'} a_{\alpha''}$	(122.01)	3
$- M_{23}$	$= a'_\alpha a''_\alpha a_x [a' a'' u] a'_x + (a' a' u) a''_x]$	(311.12)	3
$\bar{E}_{2,3}$	$= (a' a'' x) a_{\alpha'} a_x u_{\alpha'}$	(122.12)	6
$\Upsilon$	$= (a' a' a'') u_\alpha u_{\alpha'} u_{\alpha''}$	(222.30)	1
$U_{2,3}$	$= (a' a'' u) a'_{\alpha'} a''_\alpha u_\alpha u_{\alpha''}$	(213.30)	6 <sup>5)</sup>
$\bar{H}$	$= (a' a'' x) (a'' a x) (a' a' x)$	(222.03)	1
$Y_{2,3}$	$= (a' a'' x) a''_{\alpha'} a_{\alpha''} a''_x a_x$	(123.03)	6
$\Xi_1$	$= (a' a' a'') u_\alpha a_{\alpha'} a_{\alpha''}$	(322.10)	3
$G_1$	$= (a' a'' u) a'_{\alpha''} a_{\alpha''} a_{\alpha'} a''_{\alpha'}$	(133.10)	3 <sup>6)</sup>
$\bar{G}_1$	$= (a' a'' x) a''_{\alpha'} a''_\alpha a'_\alpha a'_{\alpha''}$	(233.01)	3 <sup>7)</sup>

Die Methode der Irreduzibilitätsbeweise ist dieselbe wie in § 1.

Die Formen  $L, V, \Omega, X, G, U, Y$  sind irreduzibel, denn wären sie reduzibel, so wären auch  $A_{11}, B, \bar{N}, C, D, D, \Delta$  (s. § 1), die aus

<sup>1)</sup> Die Summe der drei  $V$  ist, wie man sogleich sieht,  $= L. u_x$ .

<sup>2)</sup> Die Summe der drei  $\bar{V}$  ist reduzibel.

<sup>3)</sup> Bei CIAMBERLINI heissen diese 6 Formen  $P_1 P_2 P_3 \Pi_1 \Pi_2 \Pi_3$ .

<sup>4)</sup> Bei CIAMBERLINI heissen diese 6 Formen  $E_{23}, E_{31}, E_{12}, E'_{23}, E'_{31}, E'_{12}$ .

<sup>5)</sup> Bei CIAMBERLINI heissen diese 6 Formen  $U_{23} U_{31} U_{12} U'_{23} U'_{31} U'_{12}$ .

<sup>6)</sup> Die Formen  $G$  und  $\bar{G}$  finden sich nicht in der Ciamberlinischen Tafel (a. a. O. (p. 153). Das ist aber offenbar ein Schreib- oder Druckfehler, denn auf S 145 ist die Form  $G$  genannt unter den "Forme con un determinante fattore"; bei den reduzibelen Formen p. 148 wird  $G$  nicht genannt (d. h. sie wird zu den "forme fondamentale" gerechnet); in der Tafel der "forme fondamentale" S. 153 wird sie nicht genannt, wohl aber mitgezählt, und in den geometrischen Anwendungen S. 157 taucht sie wieder auf. Vgl. SEELIG, Monatshefte f. Math. u. Phys. 29, p. 265, Fussnote 21.

<sup>7)</sup> Bei BAKER finden sich ausserdem noch die Formen (810)<sub>2</sub>, (911), (1010), die reduzibel sind nach CIAMBERLINI (p. 151 g, p. 149 c, p. 151 g).



den erstgenannten durch Identifizierung von 2 der 3 Kegelschnitte entstehen, reduzibel.

Für die beiden Formen  $E_{2,3}$  und  $E_{3,2}$  findet man durch Spezialisierung:

$$\begin{aligned} [E_{2,3}]_{1=2} &= C_{2,3} = \text{irreduzibel}; & [E_{2,3}]_{1=3} &= \text{reduzibel}; \\ [E_{3,2}]_{1=2} &= \text{reduzibel}; & [E_{3,2}]_{1=3} &= C_{3,2} = \text{irreduzibel}; \end{aligned}$$

Daraus folgt: Es kann weder  $E_{2,3}$ , noch  $E_{3,2}$ , noch auch eine lineare Kombination der beiden, reduzibel sein, denn sonst wäre auch eine der Formen  $C$  reduzibel.

Die dualistische Betrachtung gilt für  $\bar{E}_{2,3}$  und  $\bar{E}_{3,2}$ .

Für die übrigen Formen werde ich alle apriori möglichen homogenen Reduktionsformeln aufstellen. Dabei ist folgendes zu beachten. Wenn eine Komitante  $K_{2,3}$  symmetrisch ist bezüglich der Formen  $f_2$  und  $f_3$ , so kann man in einer Reduktionsformel für diese Komitante rechts die Indizes 2 und 3 überall vertauschen, ohne dass die Formel ihre Geltung verliert. Bildet man dann die halbe Summe der beiden Ausdrücke, so fallen alle alternierenden Glieder heraus, die symmetrischen bleiben stehen, und die anderen Glieder bilden Gruppen von je zwei ähnlichen mit gleichen Koeffizienten. Ist hingegen  $K_{2,3}$  alternierend bez. 2 und 3, so kehren sich die Verhältnisse gerade um: man bildet die halbe Differenz, die symmetrischen Glieder heben sich weg, die alternierenden bleiben. usw. Diese beiden Fälle werden mit  $s$  (symmetrisch) und  $a$  (alternierend) bezeichnet. In den jetzt folgenden Formeln sind diese beiden Operationen bereits ausgeführt; beispielsweise sind in der ersten Formel die letzten beiden Glieder mit gleichen Koeffizienten versehen.

- (1) $s$   $S_{2,3} = \lambda f_1 L + \mu (f_2 A_{1,13} + f_3 A_{1,12})$
- (2) $s$   $\Sigma_{2,3} = \lambda (F_{1,2} A_{2,33} + F_{1,3} A_{2,22}) + \mu (F_{2,2} A_{1,33} + F_{3,3} A_{1,22})$
- (3) $s$   $\bar{A} = \lambda L^2 + \mu (A_{1,13} A_{2,33} + A_{1,12} A_{2,22} + A_{2,21} A_{1,31})$
- (4) $s$   $\bar{V}_1 = \lambda L^2 u_x + \mu (A_{1,12} A_{2,33} + A_{1,13} A_{2,22}) u_x + \nu A_{1,22} A_{1,33} u_x + \rho A u_x + \sigma L V_1^{-1}$
- (5)  $P_{2,3} = \lambda L A_{2,33} u_x + \mu A_{1,22} A_{2,33} u_x + \nu A_{1,33} A_{2,22} u_x + \rho A_{2,33} V_1 + \sigma A_{2,33} V_2$
- (6)  $H = 0$
- (7)  $I = 0$
- (8)  $O_1 = 0$
- (9) $s$   $T_1 = \lambda (E_{2,3} + E_{3,2}) + \mu O_1 u_x$
- (10) $s$   $M_{2,3} = \lambda (A_{1,12} N_{1,3} - A_{1,13} N_{1,2})$
- (11) $a$   $\mathbf{r} = \lambda (O_1 F_{2,3} + O_2 F_{3,1} + O_3 F_{1,2}) + \mu L H$
- (12) $a$   $\bar{H} = \lambda (f_1 \Omega_1 + f_2 \Omega_2 + f_3 \Omega_3) + \mu L H$

<sup>1)</sup> Das Glied  $\tau L(V_2 + V_3)$ , das noch möglich wäre, ist gleich  $\tau L u_x - \tau L V_1$ , und somit in anderen Gliedern der Gleichung aufzunehmen.

$$(13)a \Xi_1 = \lambda L O_1 + \mu (A_{112} O_2 + A_{111} O_3)$$

$$(14)a \bar{G}_1 = \lambda L \Omega_1 + \mu (\Omega_2 A_{223} + \Omega_3 A_{232}) + v (A_{122} X_3 + A_{132} X_2).$$

(6), (7). (6) und (7) gelten nicht, denn  $H$  und  $I$  stellen JACOBIANA und CAYLEYANA des Bündels  $\lambda_1 f_1 + \lambda_2 f_2 + \lambda_3 f_3$  dar<sup>1)</sup>.

(1). In (1) setze man  $a_x' = v_x$  (kurz:  $a = v$ ). Es verschwinden dann alle Ausdrücke die ein Symbol  $a$  enthalten. Daher  $S_{23} = 0$ ,  $A_{112} = 0$ ,  $A_{111} = 0$ . Weiter ist dann  $f_1 \equiv 0$ ,  $L \equiv 0$ . Daraus folgt  $\lambda = 0$ . Zweitens wähle man  $x$  in einem der 4 Schnittpunkte von  $f_2$  und  $f_3$ . (1) wird dann  $S_{23} = 0$ . Geometrisch würde das bedeuten, dass die Tangenten in  $x$  zu  $f_2$  und  $f_3$  konjugiert sind bezüglich  $f_1$ , was nicht immer der Fall ist, weil  $f_1$  ganz beliebig.

(2). In (2) setze man  $a' = v$ . Dann wird  $\Sigma_{23} = 0$ ,  $F_{22} = 0$ ,  $A_{112} = 0$ ,  $A_{322} = 0$ ,  $F_{13} \equiv 0$ ,  $A_{233} \equiv 0$ . Das ergibt  $\lambda = 0$ . Weiter verläuft der Beweis dualistisch entsprechend zu (1).

(3). In (3) setze man  $a' = v$ ,  $a'' = w$ . Das ergibt in derselben Weise wie bei den früheren Beweisen  $\lambda = 0$ . Setzt man nur  $a' = v$ , so findet man  $u = 0$ . (3) wird damit  $A = 0$ . Dualistisch müsste dann auch  $L = 0$  sein, was falsch ist.

(4). In (4) setze man zuerst  $a' = v$ ,  $a' = w$ ,  $a'' = s$ . Dann findet man

$$0 = \lambda (v w s)^4 u_x + \sigma (v w s)^3 (w s u) v_x.$$

Da aber die Linien  $u$  und  $v$  unabhängig sind, müssen die Koeffizienten von  $u_x$  und  $v_x$  einzeln verschwinden, somit  $\lambda = 0$ ,  $\sigma = 0$ . Oder:  $\bar{V}_1$  enthält den Faktor  $u_x$ . Daraus folgt aber dualistisch, dass auch  $V_1$  den Faktor  $u_x$  enthalten müsste, was nicht der Fall ist.

(5). In (5) setze man  $a' = v$ .  $P_{23}$ ,  $A_{122}$  und  $A_{232}$  verschwinden dann. Nach Division durch  $A_{233}$  erhält man:

$$0 = \lambda (a a'' v)^3 u_x + \varrho (a v a'') (v a'' u) a_x + \sigma (a v a'') (a'' a u) v_x.$$

Setzt man hier  $a = s$ ,  $a' = w$ , so findet man eine lineare Abhängigkeit der drei Linien u.s.w. welche aber ganz beliebig sind. Das ist nur dann möglich, wenn alle Koeffizienten Null sind, also wenn  $\lambda = 0$ ,  $\varrho = 0$ ,  $\sigma = 0$ . Daraus folgt dass  $P$  den Faktor  $u_x$  enthält. Setzt man in  $P$  aber  $a = v$ , so zerfällt  $P$  in zwei nichtverschwindende Faktoren, der eine linear in  $u$ , der andere in  $x$ . Diese beiden Tatsachen sind unvereinbar.

(8). Die zu (8) duale Formel  $\Omega = 0$  gilt nicht, daher kann (8) auch nicht gelten.

<sup>1)</sup> Siehe CLEBSCH-LINDEMANN, a.a.O., oder besser BAKER, a.a.O., wo man die geometrischen Untersuchungen von CLEBSCH, ROSANES, usw. über die Figur dreier Kegelschnitte zusammengestellt findet.



(9). In (9) setze man  $a = v$ . Die rechte Seite verschwindet, und man erhält

$$(v a' a'') (a'' u v) (a' u v) \cdot v_x = 0$$

oder

$$(v a' a'') (a'' u v) (a' u v) = 0$$

und somit: die beiden Polaren des Punktes  $\overline{uv}$  bezüglich  $f_2$  und  $f_3$  schneiden sich auf  $v$ . Das ist aber offenbar nicht immer der Fall, da diese beiden Polaren nach Wahl der Linien  $u$  und  $v$  noch beliebig gewählt werden können.

(10) In (10) setze man  $a' = v$ ,  $a'' = w$ , und erhält

$$v_x w_x \cdot \{a_x (a w u) \cdot v_x + a_x (a v u) \cdot w_x\} = \\ = \lambda \{v_x^3 \cdot (a w u) a_x \cdot w_x + w_x^3 \cdot (a v u) a_x \cdot v_x\}.$$

Da diese Gleichung für jedes  $u$  gelten muss, so müssen die Koeffizienten von  $(a w u) a_x$  und  $(a v u) a_x$  jeder für sich Null sein. Folglich wäre

$$v_x w_x \cdot w_x - \lambda \cdot w_x^3 \cdot v_x = 0$$

was, wegen der Unabhängigkeit der Linien  $u$  und  $v$  unmöglich ist.

(11) In (11) setze man  $a = v$ ,  $a' = w$ ,  $a'' = s$ , und erhält  $\mu = 0$ . Setzt man nur  $a = v$ ,  $a' = w$ , so findet man  $\lambda = 0$ . (11) wird damit  $\gamma = 0$ ; die dualistische Formel (7) gilt aber nicht, daher kann auch (11) nicht gelten.

(12) In (12) setze man  $a' = v$ ,  $a' = w$ ,  $a'' = s$ , und erhält  $\mu = 0$ . Setzt man nur  $a = v$ , so findet man  $\lambda = 0$ . (12) wird damit  $\bar{H} = 0$ . Die duale Formel gilt aber nicht, daher kann auch (12) nicht gelten.

(13). In (13) setze man  $a' = v$ ,  $a'' = w$ , und findet  $\lambda = 0$ . Setzt man nur  $a' = v$ , so findet man  $\mu = 0$ . (13) wird damit  $\Xi = 0$ . Die dualistische Formel gilt aber nicht, daher kann auch (13) nicht gelten.

(14). In (14) setze man  $a = v$ , und findet

$$\lambda (v a' a'')^2 \cdot (a' a'' x) v_{x'} v_{x''} + r \{v_{x'}^3 (v a' a'') a''_{x'} v_{x''} a'_x + v_{x''}^3 (v a' a'') a'_{x''} v_{x'} a''_x\} = 0.$$

Jetzt wähle man für  $v$  eine der gemeinsamen Tangenten von  $f_2$  und  $f_3$ . Dann ist  $v_{x'}^2 = 0$ ,  $v_{x''}^2 = 0$ ,  $(v a' a'')^2 \equiv \neq 0$  (denn  $(v a' a'')^2$  ist nur dann Null, wenn  $v$  die beiden Kegelschnitte in harmonischen Punktpaaren schneidet),  $(a' a''_x) v_{x'} v_{x''} \equiv \neq 0$  (denn diese Form ist nur dann identisch Null in  $x$ , wenn die Verbindungsline der beiden Pole, oder Berührungspunkte von  $v$ , unbestimmt wird). Also  $\lambda = 0$ . Nimmt man sodann für  $v$  eine beliebige Tangente von  $f_3$ , die nicht zugleich Tangente von  $f_2$  ist, so wird  $v_{x'}^2 = 0$ ,  $v_{x''}^2 \neq 0$ , während man geometrisch leicht einsieht, dass  $(v a' a'') a''_{x'} v_{x''} a'_x \neq 0$ . Also  $r = 0$ . Jetzt ist die Formel (14) homogen in  $\alpha$  und  $\alpha$ ; sie kann daher dualisiert werden ohne dass Faktoren  $\frac{4}{3} \alpha_x^2$  hinzutreten. Aus der Irreduzibilität von  $\zeta$  folgt dann ihre Unmöglichkeit.

**Astronomy.** — "*On the magnitude equation of OSTHOFF's estimates of star-colours*". By EJNAR HERTZSPRUNG.

(Communicated at the meeting of February 24, 1923).

In *Annalen van de Sterrewacht te Leiden* Vol. XIV, Part 1, p. 14; 1922 I have noticed an unexplained magnitude equation for the derived  $c_2/T$  values of stars of the spectral classes AO, A2, A3 and A5. Now the  $c_2/T$  values used i.e. depend for about 58 percent of the total weight on direct colour estimates. A redetermination of the magnitude equation of those estimates is therefore very desirable. The opportunity for this is given by the new catalogue of OSTHOFF (*Specola Astronomica Vaticana* Vol. VIII; 1916) extending his estimates with the 4 inch refractor one magnitude farther viz. to about 6<sup>m</sup>. A card catalogue was made containing the hour of R. A., the degrees of declination, the spectrum of the new Draper Catalogue H.D. (taken from the Index Catalogue, Spec. Astr. Vat. IX; 1917), the magnitude to one tenth and the estimated colour. The cards were divided into groups according to spectrum. After some trial the subdivisions of spectral class were combined in the way as shown in Table 1. For each of the 6 combined groups corresponding values of mean magnitude and mean estimated colour are given. On the accompanying diagram the figures of Table 1 are represented graphically.

The most striking fact is, that the estimated colour does not, as hitherto adopted <sup>1)</sup>, increase continuously with decreasing apparent brightness but shows a maximum in the neighbourhood of 4<sup>m</sup> or 5<sup>m</sup>. Especially for the white stars the decrease in estimated colour between 5<sup>m</sup> and 6<sup>m</sup> is very marked. This is nothing more, than should be expected from the known peculiarities in colour-conception by the human eye. If the spectrum of the sun is made to increase in intensity starting just below the limit of visibility, the blue and green portion will appear first, but without showing any colour, until by still greater intensity the colours green and blue are

<sup>1)</sup> A. Pannekoek, Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings of the Meeting of Saturday October 27, 1906, and E. HERTZSPRUNG, Zeitschr. für wiss. Photographie Bd. 5, 100; 1907.



seen. On the other hand the red end of the spectrum will appear red, as soon as it is perceived. By very great intensities the colours will again loose in saturation <sup>1)</sup>. The magnitude equation found for OSTHOFF's colours is in accordance with these facts.

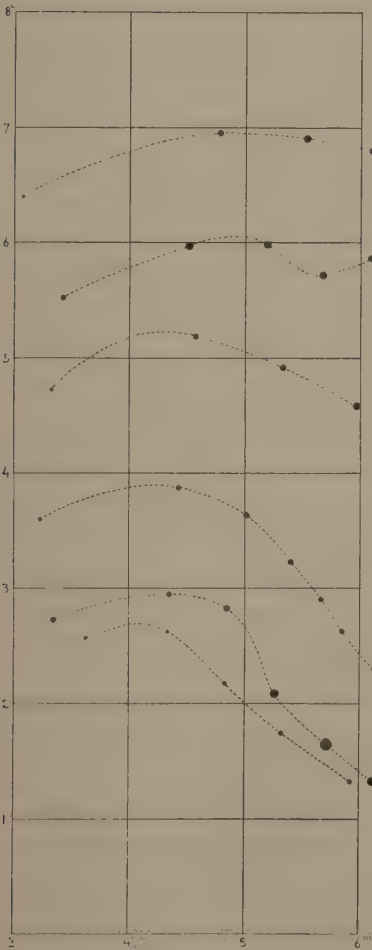


Figure 1.

TABLE I.

B3, B5			B8, B9, A0, A2, A3			A5, F0, F2, F5			F8, G0, G5			K0			K2, K5, M5, M		
n	m	c	n	m	c	n	m	c	n	m	c	n	m	c	n	m	c
18	3.63	2.57	65	3.35	2.73	30	3.24	3.60	23	3.32	4.72	51	3.42	5.52	22	3.07	6.40
23	4.34	2.63	59	4.35	2.95	51	4.43	3.87	61	4.58	5.19	106	4.51	5.96	71	4.78	6.95
38	4.83	2.18	84	4.85	2.83	73	5.01	3.64	77	5.33	4.92	105	5.19	5.98	99	5.53	6.90
48	5.32	1.75	145	5.26	2.09	63	5.40	3.24	108	5.97	4.59	107	5.66	5.72	87	6.09	6.80
48	5.92	1.32	104	5.55	1.75	52	5.66	2.90				105	6.09	5.86			
			173	5.80	1.59	59	5.85	2.63									
			132	6.11	1.33	70	6.14	2.30									

<sup>1)</sup> E.g. the wire of the electric lamp behind the darkroom glass, only letting red light through, appears yellow.

The results obtained are able to clear up the discrepancies cited above from Leiden Ann. XIV. At the same time they form an instructive example of the unsafety of extrapolation, as just at about  $5^m$ , which was the limit of brightness of the stars concerned in Leiden Ann. XIV, the magnitude equation of the estimated colour changes its character.

The above considerations rest on the assumption, that stars of the same spectrum do not show any systematic change of effective temperature with apparent magnitude. As long as we have no other reliable colour-equivalents of these stars, this seems to be the most plausible supposition, which can be used.

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**Anatomy.** — “*On the development of the shoulder-girdle and episternum in Reptiles*”. By CHR. VAN GELDEREN. (Communicated by Prof. L. BOLK).

(Communicated at the meeting of December 30, 1922).

In comparative anatomy we distinguish in the primary shoulder-girdle of most Sauria the scapula and suprascapula, coracoid, epicoracoid and procoracoid. Procoracoid and coracoid are usually homologised with the similarly-named portions of the shoulder-girdle of the Urodela and Anura. This was long ago contested by GÖTTE<sup>1)</sup>. According to him there is nothing in the ontogenesis to justify such an independence being attributed to the so-called procoracoid of the Sauria, for he holds that all the parts of the ventral portion of the primary shoulder-girdle (in *Unemidophorus*) develop from one massive formation. The procoracoid of the Sauria, therefore, he says, will not originate as a free cranio-ventral process of the coracoid, to unite with it ventro-medially into a ring, as GÖTTE found it in Anura, and as in comparative anatomy it is frequently termed with respect to the Sauria. Although such a development was observed at a later date by WIEDERSHEIM<sup>2)</sup>, BROOM<sup>3)</sup> and BOGOLJUBSKI<sup>4)</sup> in a few other Sauria also, no hand-or text-books (with the exception of that by WIEDERSHEIM) make any reference to this. It is this which has led to the present article, treating of the development of the primary as well as the secondary shoulder-girdle (including episternum).

In intimate connection with the question as to the ontogenesis of the episternum is another, namely, that of the development of the clavicle. And attention will also be devoted to this in the following lines.

The episternum, for the first data of the development of which we have to thank RATHKE<sup>5)</sup>, was seen by the latter to originate

1) A. GÖTTE, *Archiv. f. mikrosk. Anat.* Bd. XIV, 1877.

2) R. WIEDERSHEIM, *Das Gliedmaszenskelett der Wirbelthiere*. Jena, 1892.

3) R. BROOM, *Trans. South. Afric. Philos. Soc.* Vol. XVI, Pt. 4, 1906.

4) S. BOGOLJUBSKI, *Zeitschr. f. Wissensch. Zool.* Bd. 110, 1914.

5) H. RATHKE, *Ueber den Bau und die Entwickl. des Brustbeines der Saurier*. Königsberg 1853.

unpaired between the medial ends of the clavicolae. GÖTTE holds the opinion that, also on account of its paired formation, the episternum develops from a part of the clavicular formation which is bent caudally. Moreover, in his opinion, the clavicle originates as a blastemic process of the primary shoulder-girdle. GEGENBAUER <sup>1)</sup>, on the contrary holds that the connection of the clavicle and shoulder-girdle is a secondary one. HOFFMAN <sup>2)</sup> observed the paired development of the episternum in the crocodile, and also on the basis of GÖTTE's researches, he speaks of a clavicular sternum. WIEDERSHEIM was not able to find any real genetic connection of the episternum with the clavicle either in *Lacerta* or in *Crocodilus*, although he succeeded in recognizing the clavicle, the embryonal existence of which GÖTTE had already surmised in a rudimentary form. As regards the relation between the clavicle and the scapulo-coracoideum, WIEDERSHEIM shares GÖTTE's opinion. SCHAUINSLAND <sup>3)</sup> did not find in *Sphenodon* any primary connection of episternum and clavicle in stadia where the medial portion of the latter contained no bone as yet. Besides a primary connection of clavicle and scapulo-coracoideum BOGOLJUBSKI mentions a paired formation of the episternum, in which the ossification takes place from paired centra. Of the genetic relations of clavicle and episternum he gives no details.

None of the researchers ever found any cartilage in episternum and clavicle. GÖTTE and WIEDERSHEIM, however, describe a form of ossification which is strongly suggestive of the formation of perichondral bone round about a nucleus of cartilage. The bony clavicle, they say, first canaliculate and afterwards cylindrical, enclosing a soft medullar cord, just like a cartilaginous process. SCHAUINSLAND and BOGOLJUBSKI specially mention to have found no trace of such a peculiar ossification process. According to these writers the medullar cavity is produced by osteoklastic action.

I had for my investigations seventeen embryos of the common lizard, *Lacerta agilis*, all of which I prepared in cross-sections. (Section thickness 10  $\mu$ ). Further, the collection belonging to the Anatomic Laboratory contained a dozen series of *Gongylus ocellatus* and two of *Ptychozoon homalocephalum*. The direction in which sections were made in the thorax-region depended intimately upon the age of the embryos, namely, they were all made frontal on the jaw. This, with the slight curve in the region of the neck in the older

<sup>1)</sup> C. GEGENBAUR, Untersuch. z. Vergleich. Anat. der Wirbelthiere. 2 Teil. Schultergürtel. Leipzig 1865.

<sup>2)</sup> G. K. HOFFMANN, Niederl. Archiv. f. Zoologie, Bd. V, 1879.

<sup>3)</sup> H. SCHAUINSLAND, Archiv. f. Mikrosk. Anat. u. Entw.gesch. Bd. LVI, 1900.



embryos, was practically identical with frontal on the thorax. According as the neck-curve was more pronounced in the younger embryos, the sections were made more transverse on the thorax. In the account of my observations I shall commence with *Lacerta*, as my material of this was the most complete.

Fig. 1a shows the shoulder-girdle of *Lacerta agilis* spread out in one flat plane, whereby the sternum and episternum have been left in position in order to show the relative positions. Fig. 1b shows only the primary shoulder-girdle.

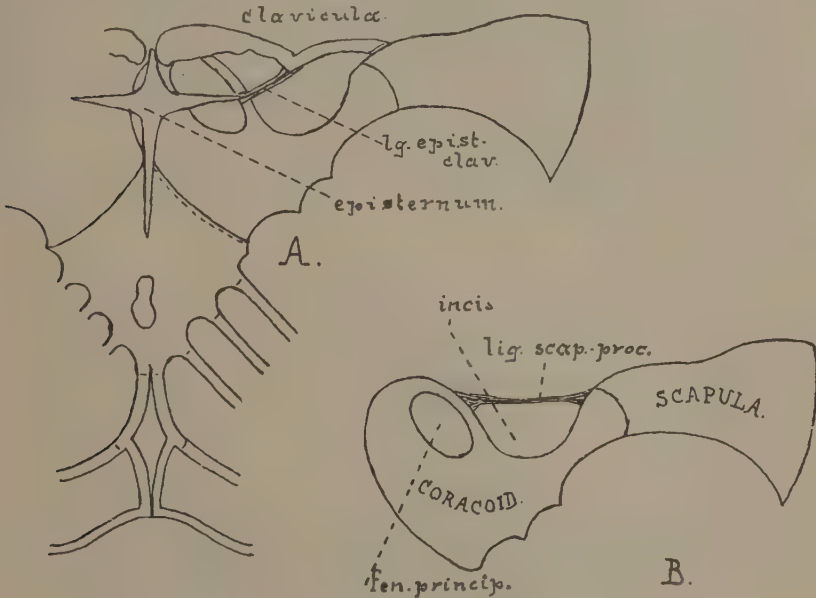


Fig. 1. Sternum and clavicula shoulder-girdle of *Lacerta agilis*.

The primary shoulder-girdle, i. e. the cartilaginous preformation, consists of a dorsal portion: the scapula and the non-ossifying large supra-scapula, and a ventral portion, viz. the coracoid, in which we usually distinguish three parts: coracoideum, s. str., procoracoid and epicoracoid. They surround an oval opening, the fenestra coracoidea principalis (FÜRBRINGER)<sup>1)</sup>. Besides this cranial to the fossa glenoidalis humeralis, there is generally another fine canal, through which the n. musc. sopracoracoidei runs. This canal will henceforth never be counted among the coracoidal fenestrae (many reptiles possess more than one fenestra<sup>1)</sup>). The cranial border of the primary shoulder-girdle exhibits a deep incisura scapulo-procoracoidea which is bridged by a strand of connective tissue, lig. scapulo-procoracoideum. The cora-

<sup>1)</sup> M. FÜRBRINGER, Jena'sche Zeitschr. Bd. 34, 1900.

coideum is received diarthrotically in the sulcus articularis coracoidealis sterni. The clavícula is connected syndesmoticly with the suprascapula. Between the medial extremities of the claviculæ the cranial point of the dagger-like episternum interposes. The latter lies mainly cranial to the sternum; a small part, however, lies ventral to the sternum and is quite separated from it by connective tissue.

The youngest embryo that I was enabled to examine, *Lacerta* ag. D. (N. T.)<sup>1)</sup> about 22), possessed no shoulder-girdle yet. Only in the inarticulated epiphysal limb was a central blastema. Besides the primary shoulder-girdle, also the clavicle was lacking.

In the embryo *Lacerta* ag. S. (N. T. about 24) the central blastema of the superior limb has extended proximally as a blastematic formation of the shoulder-girdle as yet very difficult to define. There is no trace yet of the clavícula.

The embryos *Lacerta* ag. E. and F. (N. T., about 26) contain a well defined shoulder-girdle which still consists entirely of dense mesenchyme.

Any clavicular formation is still lacking. In the humeral formation there is already praeochondrium. The line of demarcation of the coracoid with respect to the growing sternal formation is much more obscure than it was in embryo S. Specially noteworthy is the fact that the formation of the shoulder-girdle, apart from the nerve-canal, one solid whole.

Embryo *Lacerta* ag. I. (N. T. about 28) is clearly in a more advanced stage of development. Cartilage is found in the humerus, which passes over proximally into praeochondrium of which also a part of the primary shoulder-girdle consists. The latter still forms one continuous whole with the humerus. In this embryo the boundary of coracoid and sternal formations has almost disappeared, a transition stadium which will speedily be followed by the formation of the definite articular cavity. In the process of the primary girdle the praeochondrium occupies the caudal region; the rest is still compact mesenchymatous, but quite homogeneous.

From the cranial border of the scapulo-coracoideum, dorsal from the humerus-formation a blastematic spur proceeds. There is also a very small fragment of bone tissue to be seen, quite dorsally close the point of attachment to the primary shoulder-girdle.

*Lacerta* ag. K. (N. T. about 29). The line of demarcation between coracoid and sternum is indicated (now permanently) by a loose mesenchymatous layer. There is an increase of praeochondrium in

<sup>1)</sup> K. PETER, Normentafel *Lacerta agilis*.

the scapulo-coracoideum. That portion, however, which is still blastematic, has lost its homogeneity. (Compare the schemata of fig. 5.) A more compact cranial border can be plainly distinguished; the ventro-medial border is also more compact than the rest of the blastema. Further, a likewise denser strip of blastema connects the cranial border with the praeochondral caudal portion. In these compacter regions there is no praeochondrium however. The blastematic spur proceeding from the cranial scapular border has become slightly longer, as also the fragment of bone lying in it. It is from this process that the clavicle develops; we shall therefore henceforth term it the clavicular process. The connection of the scapulo-coracoid and the clavicular process will be evident from the two consecutive sections illustrated in fig. 2. The left section lies cranial to the right one. In the former the ventral outgrowth of the clavicular process can be seen; in the latter the connection with the scapulo-coracoideum.



Fig. 2. *Lacerta agilis* K. Cross-section.

The dark spot at the place where the clavicular-process goes out



from the scapula shows the thickening of the cells against the bone fragment present in the following (not drawn) section.

Embryo *Lacerta* ag. G. (N.T. about 29) is distinguished from the former one by a piece of bone which has grown larger in a ventro-medial direction in the blastematic process of the clavicle, which has grown out in the same direction. The blastematic clavicular process of the scapulo-coracoid still reaches much further ventrally than the bone fragment.

Embryo *Lacerta* ag. H. (N.T. about 30). Both the form and the histological differentiation of the formation of the parts of the skeleton have undergone marked changes. The calcified cartilaginous diaphysis is surrounded by a covering of perichondral bone. The articulation humeri is indicated by a layer of thick mesenchyme which lies between the cartilaginous proximal humerus extremity and the shoulder-girdle. Cartilage is found in the scapulo-coracoid in accordance with the position of the scapula and of the later coracoidium s. str., i.e. in the dorsal and ventro-caudal parts. The ventro-cranial half consists of praechondrium and blastema, except that where, in the adult lizard, the epicoracoid, procoracoid and lig. scapulo procoracoidium are found, we find in this embryo praechondrium, and that at the place of the future fenestra principalis and of the membrana scapulo-procoracoidia, only thickened mesenchyme blastema is found. For the rest the scapula has grown out in a dorsal direction as well as the coracoid has done in wider sense in a ventral direction. The clavicular-process has grown longer ventro-medially, especially the bony nucleus lying in it. Moreover it is also striking that caudal to the bony clavicle a compact blastema-mass has developed. The significance of this will become plain later.

Embryo *Lacerta* ag. J. (N.T. about 31). The organs, the development of which are examined here, show no striking differences from embryo H. More cartilage is present in the scapulo-coracoid than before. The outline of the praechondrium against the blastema is more easily definable. The blastema, of which the bony clavicle occupies the cranial border, has increased in size but is still perfectly homogeneous. It is distinctly loose of the coracoid lying underneath it (properly dorsal to it). The schemata of fig. 6 may now be compared.

Embryo *Lacerta* ag. L. (N.T. about 31). In this specimen many of the parts still praechondral in the former embryo have become cartilaginous. The blastema, of which the bony clavicle occupies the cranial border, has increased in size, but is still homogeneous. The bony clavicle is now nearly as long as the clavicular blastema.

In the ventral medial line the clavicular-blastema of both sides are still distinctly separated.

Those parts of the coracoid which were still blastematic in the former embryos have decreased in density and have become somewhat lighter. (fenestra principalis and membr. scapulo-procoracoidea). The later lig. scapulo-procoracoideum has remained praeochondral. Pro- and epicoracoid now consist of cartilage. Fig. 3 shows four sections taken from this series (not consecutive). Section *a* contains the procoracoid, the lig. scapulo-procoracoideum and the scapula; section *b* has already passed (more caudally) through the later membrana scapulo-procoracoidea; section *c* contains also the thinner blastema which corresponds to the later fenestra principalis; section *d* finally contains only coracoideum s. str. (and scapula).



Fig. 3. *Lacerta agilis* L. Cross-section.

Embryo *Lacerta ag.* N. (N.T. about 32). The entire definite coracoid in a wider sense is now present in cartilage. In the bridging over of the incisura scapulo-procoracoidea, the praeochondrium has diminished while the blastema has increased. The thinning of the blastema corresponding to the membrana scapulo-procoracoidea and to the fenestra principalis, already seen in the preceding embryo, is continued here. The definite form of incisura and fenestra is clearly recognisable.

In the blastema which joins the clavacula caudally a still slight central thinning can be seen. Simultaneously, in the unthinned,

medial and caudal boundaries of the thinned centrum, a small trace of bone-tissue is seen, at a place almost corresponding to the crossing-point of the definite episternum. The blastematic medial ends of the claviculae are no longer sharply defined; and there is no connection yet between the two by way of the medial line.

Embryo *Lacerta* ag. O. (N.T. about 32). The changes in the primary girdle are confined here to the non-cartilaginous portions. At the place of the *incisura scapulo-procoracoidea* and of the *fenestra principalis* the thinning of the tissue is fairly complete; the blastema once present has become nearly a membrane of connective tissue. In the cranial border of the *membrana scapulo-procoracoidea* a thicker strand is distinguishable, in which a few *praeochondrium insulae* are lying, as the remains of a entirely *praeochondral* bridging. In the retro-clavicular blastema the central thinning has proceeded further. Fig. 4 shows five partial illustrations of sections from this series. Each has been drawn exactly to the medial plane. There was still loose mesenchyme between the right and left claviculae. In Fig. *a* the bony clavicula has been taken for the greater part lengthwise. In Fig. *b* only the thickened medial end of the clavicula is to be seen. Lateral to it comes a thinner blastematic region (thinned centre), still more laterally the cut caudal border. In Fig. *c* only the thinned centre with the caudal surrounding border medial and lateral to it has been reproduced. Of the clavicular bone no more traces are to be seen. Figs. *d* and *e* have been chosen caudal to the thinned centre. Fig. *e*, the most caudal, shows the last vestige of the retroclavicular blastema.

Embryo *Lacerta* ag. M. (N.T. about 33). In this one the thinning into a connective tissue membrane has been fully accomplished at the place of the *incisura scapulo-procoracoidea* and of the *fenestra principalis*. Apart from a *praeochondral insula*, the *incisura* bridging consists of a strand connective tissue, ligament. The central thinning of the blastema lying caudal to the bony clavicula has here, too, practically led to the formation of a connective-tissuemembrane. The bony episternum has grown in size. There is thus now one connected complex present, consisting of a thin bony episternal transverse bar (situated in the caudal boundary), from which a thin blastema bundle can be traced to a point ventral of the equal-sided sternal band and in which a still much thinner fragment of bone, (even broken perhaps locally) is found. Thus, for the first time, in this embryo a small piece of the episternum is met with ventral from the sternal formation. From the transverse bar a blastema bundle (likewise caudal border) runs in a lateral and cranial direction and



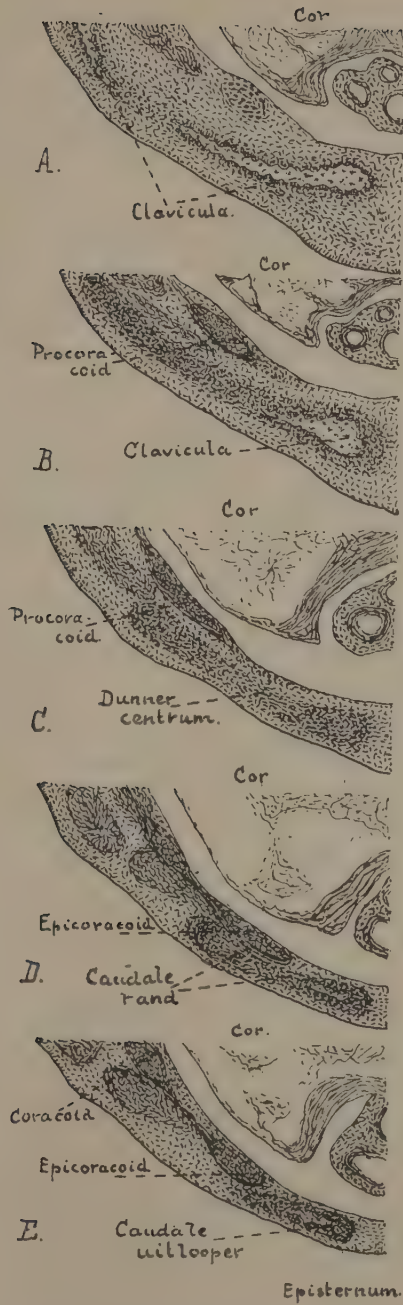


Fig. 4. *Lacerta agilis* cross-section.  
 Dunner centrum = Thinner centre.  
 Caudale rand = Caudal margin.  
 Caudale uitlooper = Caudal process.

comes to insertion at the clavicle. Finally, the medial boundary forms a blastema strip, in which the half of the little cranial point of the episternum will develop later. The complex of clavicular and episternal formations is connected with that of the other half of the body at the level of clavicle and episternal transverse bar; the caudal processes are still separated.

Embryo *Lacerta* ag. P. (N.T. about 33). In this embryo the sternal borders are already blended cranially. Apart from a commencement of calcifying cartilage, there is nothing to remark at the primary shoulder-girdle except the occurrence of a cartilaginous insula in the lig. scapulo-procoracoideum. The coracoidea have passed the medial line, and are thus partly overlapping each other. The central thinning in the episterno-clavicular blastema has completely given place to the membrana-clavicularis. In the caudal border the episternal transverse bar has elongated, and its lateral extremity is attached by ligament to the clavicle. The episternum, now grown unpaired, has also acquired a cranial point which interposes itself between the two clavicles. In cross-sections it shows traces of paired formation, (deep medial groove on the dorsal side); the paired bony formation I have not seen however. On the medial half of the clavicle a thick cranial border and a thinner caudal bone-plate can be distinguished, the latter being evidently an ossified portion of the claviculo-episternal membrane.

In embryo *Lacerta* ag. Q. (N.T. about 33—34) the cranio-caudal measurement of the episternum has attained its definite relative size. Several cross-sections show a paired cranial episternal point. This duality is merely local however. Nevertheless I take it as a proof that also this part of the episternum is formed pairedly, in which case the whole bony episternum was originally paired. In the primary shoulder-girdle the calcification has extended.

Regarding embryo *Lacerta* ag. R. (N.T. about 34—35), in which the portions of the bony skeleton discussed here have all attained their definite form, although on a small scale, there is nothing of note except that in the lig. scapulo-procoracoideum vestiges of cartilage are still to be found.

When the scapulo-coracoideum passes into praeochondrium and later into cartilage, a narrow strip of tissue remains between it and the bony clavicle at the blastema stage. We can now for the first time speak of a syndesmosis scapulo-clavicularis, although the connection between scapula and clavicle was already long present. Only with the histological differentiation of the scapulo-coracoideum is it possible to indicate the boundary region as syndesmosis.

Of *Gongylus ocellatus* I had eleven series at my disposal, but without any older stadia, such as P. Q. and R. of *Lacerta*. As I had neither a full-grown specimen nor a good illustration of the shoulder-girdle of *Gongylus*, I am forced to describe the full-grown shoulder-girdle from data taken from the literature on the subject. Of the primary shoulder-girdle the coracoid only contains a fenestra principalis (apart from the canalis nervi supracoracoidei), just as in *Lacerta*; and further the cranial border of the scapulo-coracoideum shows a deep hollow. The clavicle, viz. the thin medio-caudal portion, according to SIEBENROCK, has an extremely irregular border.

Embryo *Gongylus* oc. T. possesses a blastematic shoulder-girdle continuous with the humerus. The diaphysis humeri already contains praechondrium. No trace of the clavicle is to be seen yet. The vaguely defined scapulo-coracoideum consists everywhere of blastema of equal denseness. The sternum lies at some distance from the coracoideum. Thus this embryo, as also *Gongylus* oc. G. which shows the same degree of development, corresponds to *Lacerta* ag. S.

The embryos *Gongylus* oc. A and B are of very nearly the same age. I shall base my description on embryo A on account of its better preserved colouring. The humerus diaphysis contains cartilage, which passes proximally over into praechondrium. This continues into the scapulo-coracoideum; but is there limited to the region bordering on the humerus. For the rest the primary girdle is blastematic, only more sharply defined than in embryo T. At this stage the sternal formation (temporary) has practically become one blastematic continuum with the coracoid. From the cranial border of the scapula a blastematic clavicular process goes out in a ventral direction. In the dorsal portion of it I found already a small fragment of bone tissue. The scapulo-coracoideum still forms one compact whole. This embryo thus agrees with *Lacerta* ag. I.

Embryo *Gongylus* oc. D. (embryo C. represents the same stadium). As in *Lacerta* ag. embryo J., the scapulo-coracoideum is here largely cartilaginous (scapulo, coracoideum s. str.). Epicoracoid and procoracoid are still praechondral. Two thinned blastemic parts have appeared; they correspond to the fenestra principalis and to the incisura scapulo-procoracoidea. The latter is closed by a ligament containing praechondrium. The clavicular blastema, as also the bony clavicle lying in it, have become longer (in a ventro-medial direction). Between clavicle and the praechondral-cartilaginous scapula is a strip which is still blastematic, representing the syndesmosis claviculo-scapularis.

In the next embryo of *Gongylus* oc. E. the thinner blastematic



parts in the primary girdle have given place to thin membranes of connective tissue, or, in other words, the fenestration is complete. The lig. scapulo-procoracoideum contains praechondrium which is connected with the cartilage of the girdle only by ligament. The bony tissue in the clavicular process has increased in extent.

In the remaining older embryos there is but little that is new to be remarked about the scapulo-coracoideum, (increase in size and commencement of calcification). The further development of the clavicular formation could not be traced. In the older embryos the latter appears in the ventral body-wall, and as it is but thinly covered with the skin, it is hardly possible in the frontally cut series to define the cell-thickening under the almost tangentially cut breast-skin from the blastemic clavicular formation. For the same reason the development of the episternum could not be traced in detail. In the oldest series a paired bony episternal formation was present. (*Gongylus* oc. E. and L.). The episternal formation of one half of the body has been demonstrated by me elsewhere. (Fig. 6)<sup>1)</sup>.

*Ptychozoon homalocephalum*. Embryo A is still very young, the diaphysis humeri contains no cartilage as yet. The shoulder-girdle formation is continuous with the humerus formation. The blastematic scapulo-coracoideum is still rather vaguely outlined. The mesenchyme thickening, of which it is formed, is quite homogeneous. Nothing is to be seen yet of the fenestra principalis which occurs in the adult scapulo-coracoid; nor of the incisura scapulo procoracoidea. The bony clavicle, or even the blastematic formation of it, is still lacking.

*Ptychozoon* embryo B. Round the diaphysis-humeri lies a covering of perichondral bone. The primary shoulder-girdle shows cartilage. The more cranial portions are still praechondral (epicoracoid<sup>1)</sup>). The fenestration of the first homogeneous compact coracoideum is already fairly complete. So the conditions correspond completely to those found in *Lacerta* J. and *Gongylus* D—E.

From the cranial border of the scapulo-coracoideum the bony clavícula proceeds, connected with the scapula by syndesmosis. Joined to the clavícula, just as in *Lacerta*, is a retroclavicular blastema. Of the episternum no traces of bone are to be found yet.

The examination of the embryos of *Gongylus* and *Ptychozoon* has thus led to the confirmation of most of the facts observed in *Lacerta*, namely the origin of the fenestra principalis and of the incisura scapulo-coracoidea by reduction of parts of an originally compact primary shoulder-girdle and also the primary connection of the

<sup>1)</sup> CH. VAN GELDEREN, Proceedings. Kon. Acad. v. Wetensch. Vol. XXIV, 1922.

blastematic clavicular formation with the scapula-coracoid. Others again of the results found in *Lacerta* could not be further verified, namely, the formation of each episternum half connected with the formation of the homolateral clavicle.

After the casuistic description in the above lines, I shall now with the help of figs. 5 and 6 summarize the development of the skeleton parts.

In *Lacerta*, as well as in *Gongylus* and *Ptychozoon* the cora-

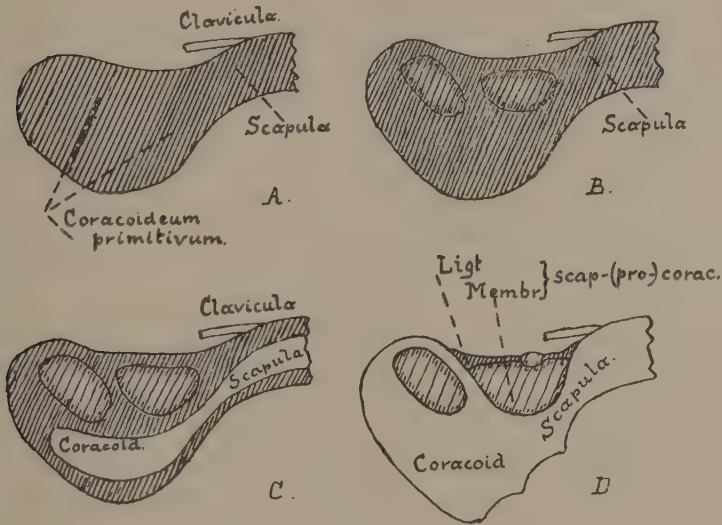


Fig. 5. *Lacerta agilis*. Schemata of the development of the coracoid.

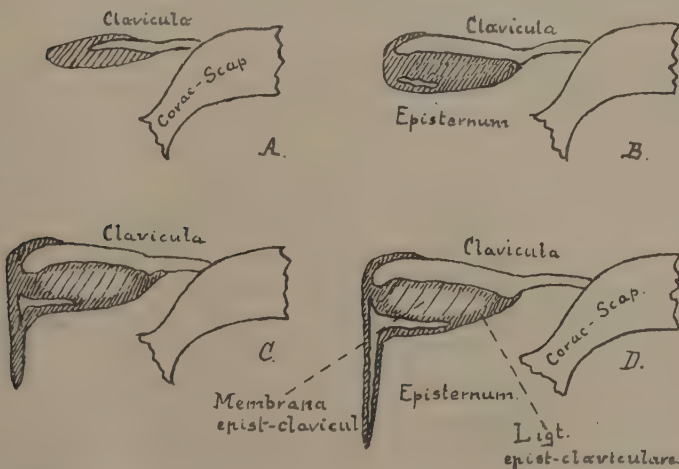


Fig. 6. *Lacerta agilis*. Schemata of the development of the secondary shoulder-girdle.

coideum in youthful stadia does not show a single trace of the fenestra principalis, and the region of the later incisura scapulo-procoracoidea still forms part of the homogeneous compact formation of the scapulo-coracoideum. When later a progressive histological differentiation occurs at the place where scapula, coracoideum s. str., epicoracoid and procoracoid will originate (formation of cartilage) this is accompanied by regressive changes at the place of the fenestra principalis and of the incisura scapulo-coracoidea, viz. a thinning of the blastema and finally reduction to a thin membrane of connective tissue. The cranial closing of the incisura does not occupy such a prominent place in these regressive changes. In the lig. scapulo-procoracoideum there are still cartilaginous insulae in the oldest embryos, which prove that this ligament is a reduced portion of the coracoid (in a wider sense). In fig. 5 the four schemata show the process of development of the coracoideum. The scapular end of the clavicle has not been hatched in each of the figures, and has been indicated in the same form. In the primary girdle hatching indicates blastema, praechondrium or connective tissue according as the hatching is more or less close. Entire absence of hatching indicates cartilage. The ab origine present nerve-canal has been omitted. The figures require no further explanation. Thus genetically both the fenestra principalis and the incisura scapulo-coracoidea, i.e. the membranes which enclose them, are parts of the shoulder-girdle. The lig. scapulo-coracoideum is, as it were, a reduced procoracoid.

As regards the episternum, in the youngest embryo in which a blastematic clavicular process was found, it was continuous with the primary shoulder-girdle. From which I deduce a genetic connection, in a sense that the clavicular blastema originates as a process of the scapulo-coracoid. It might still be opposed that the stadium in which this connection did not yet exist has not come into my hands, to which I might return that the bone in the blastematic clavicle first occurs dorsally and enlarges in a ventral direction, a symptom which, in my opinion, is strongly in favour of the genesis of the clavicle as a process of the scapulo-coracoideum.

The further development of the clavicular blastema I shall describe shortly with the help of fig. 6. In illustration *a*, already a fairly large bony clavicle is seen to be present in the blastemic clavicular process. In illustration *b* this is not more than a strip of bone lying in the cranial border of a large, for the rest homogeneous, blastema. In illustration *c* a further differentiation in the said blastema has commenced. It consists now of a centrum poorer in cells and a denser mesenchymatous border. In the latter, which represents a



portion of the episternum, a commencement of bone appears. Moreover, a thin caudally-directed blastematic process has also appeared. Finally illustration *d* shows the state of the episternum just before the right and left parts blend to one unpaired episternum. One blastema thus gives rise to one clavícula + the half of the episternum, augmented by the membrana episterno-clavicularis lying between them, which is nothing else than the reduced centrum of the original homogeneous blastema and by the lig. episterno-claviculare, that lies in the lateral border of the membrane of the same name.

If we now consider that of this joint process only that portion exists first from which the clavícula develops, I believe I may conclude that the episternum is pairedly formed from the clavicular processes. This manner of growth would imply that without the clavicle there would be no episternum, a state of matters as is seen in *Rhaptoglossa*. The conditions as found in adult crocodiles (an episternum but no clavícula) is explained by WIEDERSHEIM's discovery, namely that embryos of crocodilus contain a rudimentary clavícula. Of the peculiar manner of ossification of the clavícula, as described by GÖTTE and others, I could not find any trace.

We have still to see what comparative anatomical conclusions may be drawn from the above.

In the large comprehensive works upon comparative anatomy the opinion formulated by GEGENBAUR is expressed i.e. a great independence is ascribed to the cranial boundary of the fenestra principalis. This boundary, the procoracoid, is said to be the homologue of the similarly-named shoulder-girdle part of the Anura, Urodela and Chelonia. The procoracoid would thus occur in two main types, viz. as cranio-ventral process of the coracoideum in Urodela and Chelonia, and as cranial border of a fenestra in Anura and Sauria. *Sphenodon* has no procoracoid. The publications of GÖTTE, WIEDERSHEIM, BROOM and BOGOLJUBSKI have not been able to bring about any change in this theory. Now the coracoideum (in a wider sense) of the Sauria occurs in very different forms viz. 1<sup>st</sup> entirely without fenestrae in *Sphenodon* and *Chamaeleo*; 2<sup>nd</sup> with one fenestra, which has been named fenestra principalis on account of its frequent occurrence (FÜRBRINGER; "Hauptfenster" GEGENBAUR); 3<sup>rd</sup> with, besides the fenestra principalis, one or two more "Nebenfenster". The latter are said to have no morphological value, whereas the „Hauptfenster" has. Now we know from GÖTTE that in *Chemidophorus spec.* (3<sup>rd</sup> group: one principal and two minor fenestrae) all the fenestrae develop secondarily by regression of parts of the shoulder-girdle, or in other words, that the early-embryonal Saurian-

coracoid has the same form as that of *Sphenodon*. And, moreover, it follows from the above description of the development of the coracoid of the lizard, that the incisura scapulo-coracoidea has the same genesis as the dorsal fenestra of *Cnemidophorus*, save that in *Lacerta* the cranial border also is practically entirely reduced (except for the remains of cartilage). Thus also the coracoideum of *Lacerta* with one fenestra contains, although it seems somewhat paradoxical, a second, dorsal fenestra. Consequently the so-called procoracoid of the lizard is the sum of what is in multiple fenestrated coracoidea termed the procoracoid and mesocoracoid (mesocoracoid lies between fenestra principalis and dorsal "Nebenfenster"). By the procoracoid in the order of *Sauria* are thus understood different parts of the girdle.

This fact, as well as the development of the coracoid (taken in a wider sense), induce me to side with GÖTTE; the whole ventral portion of the primary shoulder-girdle of the *Sauria*, with or without fenestrae, corresponds merely to the coracoideum of the *Urodela* and *Anura*. Respecting the latter GÖTTE has already demonstrated that their shoulder-girdle (with one fenestra) does not acquire its definite form by fenestration, but that it passes through an *Urodelan* stage (*Rana esculenta*). The fact that the adult shoulder-girdle of *Lacerta* corresponds to that of e.g. *Rana* thus depends upon caeno-genesis. The different parts of the two shoulder-girdles are not homologous.

The crocödilia, in which a procoracoid is lacking, will thus, like *Sphenodon* and *Chamaeleo*, possess a coracoid homologous with the whole pars coracoidea of the primary girdle of *Lacerta*. In short, as far as our knowledge extends at present (regarding *Chelonia* there are no genetic data) we are not obliged in the case of any reptile to assume a procoracoid that is homologous with the procoracoid of the *Amphibia*.

GEGENBAUER postulated the homology of the episternum of the reptiles and mammals; the difference in the histological structure (reptilia: bone; mammals: cartilage or bone), and in the histogeny (reptilia: desmal, and in mammals chondral ossification) was evidently no objection, although he did consider as an objection the fact that the episternum of the *Sauria* lies ventral and that of the *mammalia* cranial from the sternum. Another weak point in the theory of this homology is that the episternum of the mammals is generally held to be a clavicular sternum, i.e. that we see in this episternum a product of the clavicularae, whereas most of the researchers who studied the episternum of the *Reptilia* did not succeed in establishing a genetic connection between the clavicle and episternum.

Only GÖTTE saw (in *Cnemidophorus*) the episternum commence as caudal process of the clavicle. Well then, the foregoing casuistic demonstration shows the genetic connection of the clavicula and episternum, even though this is not so simple in *Lacerta* as was described by GÖTTE for *Cnemidophorus*. Herewith a new point of agreement with the episternum of the mammals has been found. Further, we have seen that the episternal halves lie at first quite cranially from the halves of the breast-bone. Only later, with the commencement of the longitudinal bar does a small portion of the episternum of the *Sauria* come to lie ventrally from the sternum. The different position of the episternum thus seems to exist but partially, and it occurs secondarily. The only difficulty in homologizing the episterna of *Reptilia* and *Mammalia* is thus the histogenetic difference. And GAUPP<sup>1)</sup> has demonstrated that too much importance must not be attached to this in general.

As for the clavicle, respecting the development of which my researches confirmed its primary connection with the scapulo-coracoideum, I do not deem it advisable for the present to enter into the discussion which is being carried on as to its homology, although in the theory developed by GÖTTE (homology of the clavicle with the "Procoracoid" of the *Amphibia*, which he terms the clavicula) and of which WIEDERSHEIM,<sup>2)</sup> on the basis of his own investigations, proves himself an advocate (in the last edition of his "Vergleichende Anatomie" WIEDERSHEIM has changed his opinion, for what reason I do not know) there is undoubtedly a certain attraction.

#### SUMMARY.

1. Fenestrae in the shoulder-girdle of the *Sauria* develop secondarily, in a girdle of the type of *Sphenodon*.
2. The incisura scapulo-(pro)coracoidea is likewise a fenestra of which the cranial border, except for some cartilaginous remains, is reduced to a ligament.
3. The clavicle originates as a blastematic process from the scapulo-coracoideum.
4. The episternum proceeds from a paired formation. This formation is the product of the homolateral clavicular process.
5. As long as there are no data of the development of the girdle of *Chelonina*, there is nothing which obliges us to assume a procoracoid in any reptile, homologous with that of the *Amphibia*.

<sup>1)</sup> E. GAUPP, *Kopfskelett* in HERTWIG's *Handbuch*. Jena, 1905.

<sup>2)</sup> R. WIEDERSHEIM, *Grundriss d. Vergl. Anat. d. Wirbelthiere*. 4e Aufl. Jena 1898.



**Chemistry.** — *“Provisional Communication on Boric Acid Compounds of some Organic Substances containing more than one Hydroxyl-Group. Boron as a Pentavalent Element.”* By P. H. HERMANS. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of December 30, 1922).

The behaviour of boric acid towards hydroxyl-containing organic substances is striking in many respects. The extra-ordinary ease and rapidity with which it forms esters of the type of  $B(OR)_3$  with the ordinary saturated alcohols, also when a catalyst is absent, is a totally unexpected property for a weak, and for the rest mono-basic acid such as boric acid, and in this respect it is unequalled.

Still more interesting is the action of boric acid on the aqueous solutions of multi-valent alcohols and other substances rich in hydroxyl, such as some sugars. It has been known for a long time that these mixed solutions sometimes present a much greater hydrogen ion concentration than a solution of boric acid only. The alkaline reaction of a borax solution can even become an acid one by addition of substances such as mannite<sup>1)</sup>. Also the influence of boric acid or borates on the optical rotatory power of such substances rich in hydroxyl, was early observed. Undoubtedly these phenomena point to compounds which boric acid forms with the substances mentioned above. Several investigators have expressed their opinion about the nature of these compounds<sup>1)</sup>. Mostly it is assumed that acid boric acid esters are formed which possess a higher degree of acidity than free boric acid. Systematic attempts to find out more about these compounds through their isolation, have seldom been made, at least they have not been very successful.

In 1869 DUVE<sup>2)</sup> described a series of salts of different boro-tartaric acids, which however present the appearance of glassy, non-crystallizing masses or amorphous precipitates, the individuality of which is open to doubt. The same principle applies to most of the boro-citric acid

<sup>1)</sup> We will postpone the older and more recent literature on this subject to a following publication.

<sup>2)</sup> Vierteljahrsschr. pr. Pharm. XVIII, 321.

salts described by SCHEIBE<sup>1)</sup> in 1879 and 1880, with the exception however of a potassium salt, which was considered to have the formula  $C_{12}H_{11}K(BO)_2O_{14} \cdot 2H_2O$ , crystallizes beautifully, and to which we refer below<sup>2)</sup>.

Also among the salts of boro-salicylic acid described for the first time by JAHNS in 1878<sup>3)</sup> there are some well-crystallised compounds.

The first who inquired more systematically into the influence on the acidity of boric acid by hydroxyl-containing substances, was MAGNANINI, who published a series of papers on the influence which these substances have on the conductivity (and some other physical constants) of boric acid solutions.<sup>4)</sup> The number of compounds examined by him is very large, and he pointed out the influence of the constitution in connection with the occurrence or non occurrence of an increase of conductivity. He found a.o. that this was only observed in *o*-oxy acids, and *not* when the OH-group is somewhere else, it *was* found in aromatic *o*-oxy carbonic acids, *not* in the *m*- and *p*-isomers, it *was* found in *o*-diphenols, not in *m*- and *p*-diphenols.

These researches have been continued and extended by BÖESEKEN (and collaborators)<sup>5)</sup>, who assumed, discovered, and worked out an influence of the *steric* configuration by the side of the constitutional influence.

In his hands the Magnanini "boric acid method" became an important instrument, not only for the determination of the constitution and configuration, but also for our stereo-chemical views in general. These results reached their acme in the application of the method to the sugars and their derivatives, the isomeric tartaric acids, and the saturated cyclic vic. diols.

In his "Lagerung der Atome im Raume" VAN 'T HOFF already expressed his opinion that in the compounds which are responsible for the phenomena in question, the boron atom might be part of a ring-system, and that this ring could close only when certain condi-

<sup>1)</sup> Russ. Zeitschr. f. Pharm. **18**, 257, 289, 321; **19**, 513. Pharm. Journ. and Trans. (3) **11**, 389.

<sup>2)</sup> We have not yet been able to test entirely the records given by KLEIN in 1878 on mannite-boric acid salts of rather complicated constitution. Probably we have to do with not accurately defined substances also here.

<sup>3)</sup> Arch. der Pharm. (3) **12**, 212.

<sup>4)</sup> Z. phys. Ch. **6**, 58. Gazz. chim. Ital. **20**, 441, 448, 453; **21**, 134, 215; **22**, 541; **23**, 197. Acad. dei Lincei Rend. (4) **6a**, 411, 457.

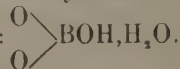
<sup>5)</sup> E.g. These Proc. Vol. XV, p. 216 (1912); Vol. XVIII, p. 1647, 1654 (1915); Vol. XXI, p. 80 (1918); Vol. XXIII, p. 69 (1920); Verslag van de gewone vergaderingen K. Akad. v. Wet. Amsterdam Dl. XXIX, p. 368, 924 (1921). Chem. Weekbl. **19**, 207. Recueil **40**, 354, 558.

tions were fulfilled. The accompanying formula was the simplest, and was used by different investigators (see e.g. ABBEGG's Handboek III pg. 43), and also served BÖSEKEN as a working-scheme. According to

this assumption one molecule of di-oxy-compound, therefore, combines with one molecule of boric acid with loss of water to a cyclic compound, which would have stronger acid properties.

Different investigators have supposed other relations as to the number of molecules combining than these to account for the physico-chemical behaviour of the mixed boric acid-polyoxyderivative-solutions, but the grounds on which these suppositions were based, are generally uncertain, and often conflicting. Up till now nothing could be said with certainty about the general type on which the acid complexes are based. The observations agree with each other only in so far that these compounds are almost completely dissociated in aqueous solution, and that their formation is favoured by increase of the concentration of the components. It further appeared from different investigations that in some cases (a.o. with substances like mannite and dulcite); several compounds of different composition must be present in the solution, of which however, it can, not be ascertained which are the typically acid ones.

In 1911 Fox and GAUGE<sup>1)</sup> described the first compound of boric acid with a multi-valent alcohol which is well crystallized. From an alcoholic solution they obtained a mannito boric acid  $C_6H_{14}O_8B$ . They do not however, say, anything about the constitution. A second compound was described by DERX<sup>2)</sup>, viz. the crystallized cis-cyclo heptane diol boric acid. He determined the boron content by titration and gave the following formula based on that  $C_7H_{14}$ :



We might consider the mannito boric acid in an analogous way as  $C_6H_{14}O_4$ :

$$: \begin{array}{c} O \\ \diagup \quad \diagdown \\ BOH, H_2O. \end{array}$$

Both alcohols increase the conductivity of the boric acid in a high degree. There were, as we see, reasons to look upon these compounds as being the strong complex acids that bring about these phenomena. The impetus for making a new attempt to ascertain the nature of the strongly acid boric acid compounds was given by the following accidental discovery. The 2.4. dimethyl pentane 2.4. diol<sup>3)</sup> when reacting on boric acid (even in very diluted

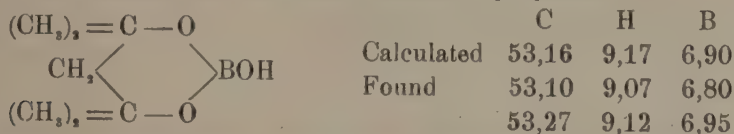
<sup>1)</sup> Soc. 99, 1075.

<sup>2)</sup> Recueil 41, 340 (1922).

<sup>3)</sup> Obtained from  $CH_3MgI$  and diacetone alcohol. Mr. LANGEDIJK drew my attention to a new method of preparation, which renders this latter substance very easily accessible. (ADAMS, Organic Syntheses 1921, p. 45).



aqueous solutions) gives a beautifully crystallizing and only slightly soluble compound, to which the following formula must be assigned as a result of analysis and examination of properties:



The compound has an exceedingly great crystallizing power, melts not entirely sharply at 100—102°, is somewhat volatile, and has a pleasant odour strongly reminiscent of saffron. It is, however, by no means a strong acid, and like boric acid it hardly colours blue litmuspaper red, and in accordance with this the said diol (which is readily soluble in water) does not bring about any increase of conductivity of the boric acid, as was to be expected from such a 1.3 diol according to the data collected by BÖESEKEN up till now.

As a result of this I believed that the really stronger acid borocomplexes must possess another structure than had been assumed so far, and this was soon confirmed. I succeeded, though only after some more difficulties, in isolating analogous and likewise only exceedingly weakly acid boron-compounds of 2.4.dimethyl hexane 2.4.diol, 2.4.pentane diol, and pinacone, likewise diols which do not appreciably influence the conductivity of boric acid. In the case of tri-methylene glycol, ordinary glycol, and cis-1.2.cyclo hexane diol the existence of compounds could be shown, but attempts to isolate them in a pure state failed<sup>1)</sup>. It is probable that all the 1.2 and 1.3 diols are able to form such compounds with boric acid, that in many cases, however, they can be separated only with great difficulty, if at all, in consequence of unfavourable solubility conditions and similar difficulties. In aqueous solution they are partially split up into their components. The compound described first, at 0° in 0,1 normal solution for 75 %. The readiness with which this compound is obtained, is owing to its slight solubility in water (4,46 g. in 100 cc. solution at 25°), which is still smaller than that of boric acid. It dissolves in diluted alkalis, probably accompanied by formation of a potassium salt, which is, however, also dissociated, as pure diol is withdrawn from the solution by ether. The liquid free diol is salted out by strong potassium hydroxide; the potassium salt itself could not be isolated as yet. In the cis. 1.2 cyclo hexane diol, however, the corresponding potassium salt is slightly soluble in an excess of strong potassium hydroxide, and crystallizes out,

<sup>1)</sup> I hope to discuss the details of the preparation in my doctor's dissertation.

before the limit of solubility of the free diol is reached. It can be obtained pure by sucking off and washing with alcohol of 96 %. It is a compound that was discovered already before by BÖESEKEN and VAN GIFFEN<sup>1)</sup> but which was not isolated and more closely examined then.

The aqueous solution of this potassium salt has an alkaline reaction, and the potassium can be determined quantitatively by titration with methyl orange, which proves anew that the corresponding complex boric acid is an exceedingly weak acid. Besides this compound  $C_6H_{11}O_4BK$ , a dipotassium compound  $C_6H_{11}O_4BK$  was obtained from very strong potassium hydroxide.

Under the same circumstances crystalline compounds can also be obtained from cis-1.2 hydridene diol, cis 1.2 cyclopentane diol, and cis-1.2 and cis 2.3 tetrahydronaphthalene diols. These compounds consist of potassium salts of either of the two types or of both, some of which could, however, not yet be obtained pure and free from potassium hydroxide being sometimes (o.a. in the case of hydridene diol) too easily soluble, both in water and in alcohol, so that they cannot be washed with one of these solvents.

It is remarkable that in the di-potassium compound of cis-cyclohexane diol boric acid both potassium atoms can be titrated with methyl orange and HCl, but that in the corresponding compound of cis-cyclopentane diol only one of the two potassium atoms can thus be titrated. We reserve a further discussion of this point till some future occasion.

We may point out here that these compounds supply us with a method to separate isomer cis- and trans- cyclic 1.2 diols from each other, the latter not giving such compounds. For in many cases the beautiful method of separation with the aid of acetone compounds found by VAN LOON<sup>2)</sup> is attended with important drawbacks, as has appeared from another investigation (to which I hope to refer later on.<sup>3)</sup>)

The fact that the formation of these cyclic and only exceedingly weakly acid compounds seems to be a general property of the 1.2 and 1.3 diols, leads to the conclusion that the more strongly acid boro-complexes, which arise in appreciable quantities only in poly

<sup>1)</sup> Recueil **39**, 183 (1920).

<sup>2)</sup> These Proc. Vol. XXIII p. 60 (1920), and proefschrift Delft p. 59; of BÖESEKEN and DERX, Recueil **40**, 519.

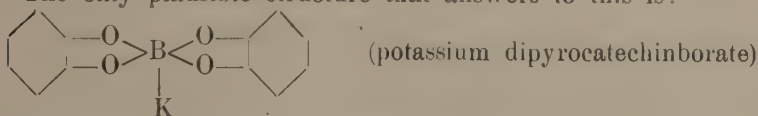
<sup>3)</sup> The new method of separation has already been successfully applied by Mr. MAAN to the methyl 1. cyclohexane 1.2 diols. The cis-diol was obtained in a much purer state than by the acetone method. as the action of acids is now fully eliminated.

oxy derivatives with "favourably" orientated OH-groups, belong to another group. In 1917 BÖESEKEN (in collaboration with OBREEN and Miss VAN HAEFTEN, *Recueil* **37**, 184) described several salts of pyro catechin boric acids of pretty complicated constitution. As the former had already for some time considered the analysis values found to be uncertain, and as the boric acid compounds described above appeared to be by no means particularly complex, there was sufficient occasion to subject the beautifully crystallized salts of pyro catechin boric acid to a renewed investigation, the more so because pyro-catechin greatly increases the conductivity of boric acid, so that accordingly the other type of compounds might be expected here. This expectation was confirmed: the potassium salt appeared to possess the formula  $C_{12}H_8O_4BK$ <sup>1</sup>).

The carbon was determined by the wet way according to the method of MEISENHEIMER, the hydrogen according to a simplified method worked out by myself, about which more will be given later. The following values were found:

C 54,28; 54,26	H 3,03	B 4,3	K 14,7
Calculated 54,14	3,00	4,1	14,7

The only plausible structure that answers to this is:



The boron is here pentavalent, or has (according to WERNER's nomenclature) the coordination value four, just as in the well-known compounds  $KBF_4$  and  $Na[B(OC_2H_5)_4]$ . The latter was obtained from  $NaOC_2H_5$  and boric acid triethyl ester<sup>2</sup>).

The free dipyro catechin boric acid can be obtained by heating the anilin salt in a vacuum of some mm. Hg. at 100—120°, in which the aniline escapes quantitatively. Mr. MEULENHOF (who has undertaken a closer investigation of these derivatives at Prof. BÖESEKEN's request), found that the acid obtained in this way can be prepared in perfectly pure condition by sublimation in vacuum at about 200°.

The potassium salt described is very little soluble in cold water, and this solution gives an alkaline reaction, probably in consequence of the fact that a dissociation in pyrocatechin and potassiumborate (possibly first in pyro catechin and mono-pyro catechin borate) sets in.

<sup>1</sup>) The erroneous constitution, given in the last-mentioned paper is owing, partly to an error of calculation that has crept in, partly to the fact that substances containing boron and being rich in C, are not easily combustible.

<sup>2</sup>) COPEAU *C.R.* **127**, 721 (1898) e.g. LIVIO CAMBI, *Acad. dei Lincei Rend* (5), **23a**, p. 244.



The potassium can, however, *not* be determined quantitatively by titration, from which it appears that we have to do here with an acid that is stronger than the mono diol boric acids described. Unchanged pyro catechin can again be withdrawn with ether from the aqueous solution.

The other complexes stronger than boric acid are probably also built up according to the type of di-pyro catechin boric acid.

So far, however, the separation of a derivative that probably belongs to this type, has succeeded only in one diol of abiphatic character, i. e. in the cis-cyclo heptane 1.2 diol. This diol was first prepared by DERX from suberic acid; he ascertained that it increases the conductivity of boric acid in a great degree, and states that he has succeeded in separating a solid boric acid compound, the B-content of which agrees with the formula  $C_7H_{14} : \overset{O}{\text{O}} > \text{BOH.H}_2\text{O}^1$ ). As only 0.2 gramme of this diol were available (prepared by DERX), I have carried out the following experiments on micro-chemical scale under the microscope.

With an almost saturated boric acid solution the diol gives rise to the formation of an oil which is only soluble in much water.<sup>2)</sup> This oil is probably the liquid diciscycloheptanediolboric acid, from which more or less accidentally DERX obtained the mono ciscyclo heptanediolboric acid as a solid substance. On addition of a little strong potassium hydroxide an aqueous suspension of this oil gives crystals of a potassium salt, while also a drop of aniline is dissolved with separation of beautiful crystal needles, which are, however, pretty readily soluble in water and other solvents.

In connection with the small quantity of material available it was better to abandon the idea of an examination of the liquid compound itself, and to try and separate one of the salts. For this purpose I chose the aniline salt to avoid the possibility that with KOH, as with the other cyclic diols, a compound of the monotype would again crystallize out. It might, however, be expected of aniline that it would give a crystallized salt only with a stronger acid.

Only a few tenths of milligrammes of the aniline salt were obtained in a sufficiently pure condition with a melting-point of about 50°. Mr. H. GRAVESTIN was so kind as to take the execution

<sup>1)</sup> Proefschrift Delft and Recueil **43**, 340 (1922).

<sup>2)</sup> As Mr. DERX communicated to me in a conversation, this oil was also observed by him, but considered as an impurity. He has obtained the solid boric acid compound described by him in a small quantity from a pretty large quantity of this oil and through rather complicated manipulations.

of a micro-elementary analysis upon him. The combustion of this boron-containing compound requires, however, special preliminary experiments, and has not yet been accomplished; the results will be published later. A determination of the boron-content yielded the following results: 9,76 mgr. were dissolved with 1 gr. of pure mannite in 10 cc. of water, and titrated with 0,0097 N barite water (under similar circumstances tested by pure boric acid) and phenolphthalein as indicator. Consumed 2,60 cc. Calculated for  $C_{10}H_{10}O_4NB$  ... 2,99 % B; found 2,8 % B.

To all probability we have here actually to do with diciscycloheptane diol boric acid aniline.

In this compound the aniline is bound still more loosely than in aniline dipyro catechin boric acid. In vacuum at room temperature it already escapes, the remaining part becoming liquid. The liquid residue becomes solid again by the addition of aniline. Also on evaporation of the aqueous solution over concentrated sulphuric acid an oil remains behind, which becomes solid again by the addition of aniline. Beside a dish with pumice saturated with aniline the salt can, however, be regained unchanged by evaporation of the aqueous solution in vacuum.

Di-ciscycloheptanediol-boric acid is, therefore probably a much weaker acid than dipyrocatechin-boric acid, and the great increase of conductivity of boric acid by pyro-catechin must, therefore, be put to the account not only of the favourable orientation of the OH-groups, but also partially to the account of the acidifying influence of pyrocatechin as such. This admonishes to caution in making comparisons with regard to the orientation of the HO-groups between diols that are not very much alike in structure, exclusively on the ground of measurements of the conductivity. This point was, indeed, already foreseen by BÖESEKEN, and was a.o. mentioned by VAN LOON<sup>1)</sup> and LIEMPT<sup>2)</sup>.

That also the increase of conductivity caused by the  $\alpha$ -oxy acids in the boric acid is probably to be attributed to the formation of complex acids built in an analogous way, we have been able to make plausible by showing that the analyses of the SCHEIBE's boro dicitric acid potassium<sup>3)</sup> and of the zincous salt of JAHNS' boro disalicylic acid are in agreement with the formulae:

<sup>1)</sup> Proefschrift Delft, p. 56.

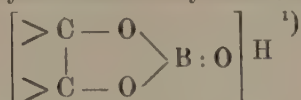
<sup>2)</sup> Recueil **39**, 359.

<sup>3)</sup> Also the free acid has been separated crystalline by SCHEIBE and by me. It is, however, difficult to purify and dry. SCHEIBE's analysis, which I have not yet checked, is in harmony with my view.



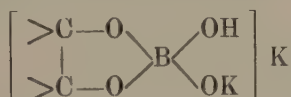


This enables the  $[(HO)_2B:O]H$  present in water to form compounds with a number of glycols and  $\alpha$ -oxy acids, of the following type:



Like boric acid these acids are very weak.

4. On the other side of the boron atom a compound can now be formed with a second molecule of diol or oxy acid with loss of water. Whether then a molecule of water is first admitted, may be left undecided for the present. The existence of dipotassium salts, to which we can assign the structure:



may possibly plead in favour of this, like the presence of an extra molecule of water in DERY's solid mono cyclo heptane diol boric acid and FOX and GAUGE's mono mannite boric acid.

A second molecule of dioxy compound is, however, received in diluted aqueous solution in appreciable quantities only when certain favourable conditions are realized, i.e. with a favourable steric situation of the hydroxyl groups in the diol or oxy acid. The tendency to the formation of a di-compound is, accordingly, smaller than that to the formation of the mono-derivatives, and the former seems, therefore, to be very sensitive to the value of the ring-tension in the ring to be formed. This fact constitutes the hypothetical foundation of BÖSEKEN's boric acid method.

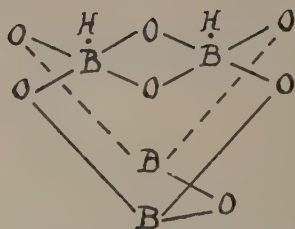
5. It is known that the poly-boric acids whose presence must be assumed in alkaline solutions, are stronger acids than ortho-boric acid. Plausible structure formulae could not be drawn up for this large series of acids as yet on the basis of trivalent boron. Possibly

they too possess the grouping  $\begin{array}{c} -O \\ -O \end{array} > B < \begin{array}{c} O- \\ O- \end{array}$ . Maintaining the as-

sumption that to each H-atom that can be replaced by metals belongs one pentavalent B-atom, the other B-atoms being trivalent, a structure schema may be constructed for a great number of poly boric acids. Tetra borix acid, which forms the foundation of borax, possesses e.g. the scheme:<sup>2)</sup>

<sup>1)</sup> In this connection it will be of importance to examine whether in the saponification of  $B(OR)_3$  by water the presence of a relatively stable intermediate product  $(RO)_2BOH$  can be shown.

<sup>2)</sup> This representation does not lay claim, of course, to be anything more than a scheme.



In conclusion it may still be mentioned that the question what place three remarkable "acid boric acid esters" described by WOHL and NEUBERG<sup>1)</sup> and also the boric acid complexes<sup>2)</sup> found by GRÜN and NOSSOWITCH, occupy in this respect must still be made a subject of investigation.

I may still be allowed to express my great indebtedness to Prof. BÖSEKEN for the kind interest which he evinced in this investigation carried out in his laboratory.

*Delft, December, 1922.      Organic Lab. of the Technical Univ.*

<sup>1)</sup> Ber **32**, 3488 (1899).

<sup>2)</sup> Sitz. Ber der Akad. der Wiss. Wien M. N. Cl. **125**, 2B, 171 (1916).

**Chemistry.** — "*The Electro-viscous Effect in Rubbersol.*" By Prof. H. R. KRUYT and W. A. N. EGGINK.

(Communicated at the meeting of January 27, 1922).

1. Researches on agarsol<sup>1)</sup> have taught that the relation<sup>2)</sup> between the charge of dispersed particles and the viscosity of the dispersed system manifests itself clearly in those sols in which the charge can be considerably modified without the colloid system as such being annihilated, i.e. in those systems of which the stability does not only depend on their charge, but in which also hydration (more general: solvation) protects the system. The conceptions about the stability of the lyophile sol may be applied throughout the territory of the emulsoids<sup>3)</sup>, at least when water is taken as the substance in which the dispersion takes place. Our attention was, however, drawn by a remark on p. 570 of O. DE VRIES' *Estate Rubber*<sup>4)</sup>, where it is stated that increase resp. decrease of the viscosity of a benzene rubber solution is brought about by shaking it with a few drops of a solution of alkali resp. of acid or salt.

As it seems as if this is a question of an electro-viscous effect, we have examined what influence electrolytes have on the viscosity of solutions of rubber in benzene.

2. Sols were used prepared in the following way: 1 gr. of a certain crèpe-rubber was added to 300 cm. of benzene, after 24 hours it was carefully shaken, and the sol was poured through a folded paper filter. Then benzene solutions of the electrolytes were made; the liquids which were to be examined viscosimetrically, were prepared by mixing a volume of sol with a volume of the solution of the electrolyte (resp. a volume of benzene, for the zero-standard); or as far as the measurement of rubberless liquids are concerned by diluting electrolyte solutions with benzene, as they were diluted with sol just before. At the

<sup>1)</sup> H. R. KRUYT and H. G. DE JONG, *Z. physik. Chem.* **100**, 250 (1922).

<sup>2)</sup> M. VON SMOLUCHOWSKI, *Koll. Z.* **18**, 190 (1918). We prefer the term electro-viscous to quasi-viscous, which v. SMOLUCHOWSKI uses, but which may give rise to misunderstanding.

<sup>3)</sup> H. R. KRUYT, *Koll. Z.* **31**, 338 (1922).

<sup>4)</sup> Batavia 1920.



beginning and at the end of every series the electrolyte-free mixture was measured, and when there was a difference, a correction was applied to the intermediate values. The measurements have been performed in an OSTWALD viscosimeter <sup>1)</sup> and at 25°.

In the subjoined tables the concentrations given are end-concentrations, the viscosity of benzene is put at 1.000,  $\eta_e$  is the viscosity of an electrolyte solution,  $\eta_{s+e}$  that of a rubber sol with equal electrolyte concentration. The relation of these quantities is given under  $\frac{\eta_{s+e}}{\eta_e}$ , after the said correction for the time reaction has been applied.

TABLE I.  
Influence of benzoic acid on the viscosity of rubbersols.

Conc. Benzoic acid mMol p. L.	Viscosity benzene + benzoic acid $\eta_e$	Viscosity rubber + benzoic acid $\eta_{s+e}$	$\frac{\eta_{s+e}}{\eta_e}$ corrected
0	1.000	1.698	1.698
6	— <sup>2)</sup>	1.635	1.633
12	— <sup>2)</sup>	1.601	1.598
24	— <sup>2)</sup>	1.584	1.577
48	1.010	1.565	1.552
96	1.018	1.559	1.533
192	1.036	1.574	1.522
0	1.000	1.695	1.698

In fig. 1 these results are represented graphically. Corresponding determinations have been carried out with acetic acid, hydrochloric acid, sulphuric acid, sulphuretted hydrogen and mercury chloride. Essentially the results are the same, the viscosity reducing action alone is different; most for hydrochloric acid, in which already  $1\frac{1}{4}$  mMol per litre reduces the viscosity from 1,573 to 1,486

Ammonia shows a very remarkable behaviour; the results are recorded in table II.

<sup>1)</sup> With observance of all precautions according to H. G. BUNGENBERG DE JONG, Rec. Trav. chim. Pays Bas **43**, 1 (1923).

<sup>2)</sup> Interpolated between the values for 0 and 48 mMol per l.

The viscosity of the  $\text{NH}_3$ -benzene mixtures ( $\eta_e$ ) did not appreciably differ from that of benzene.

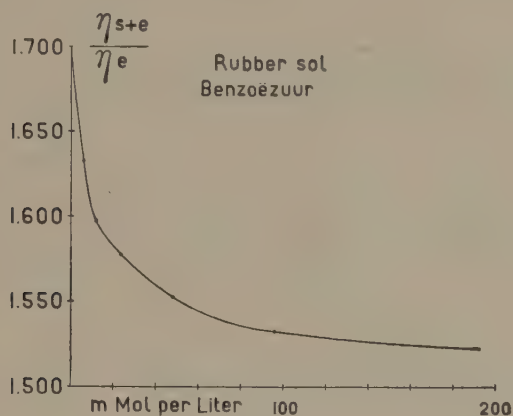


Fig. 1.

TABLE II.  
Influence of ammonia on the viscosity of rubbersols.

Conc. ammonia mMol p. L.	Viscosity rubber + $\text{NH}_3$ $\eta_{s+e}$	$\frac{\eta_{s+e}}{\eta_e}$ corrected
0	1.608	1.608
0.37	1.616	1.616
0.75	1.622	1.621
1.49	1.625	1.624
2.98	1.622	1.620
5.96	1.620	1.618
11.92	1.620	1.618
23.85	1.621	1.618
0	1.611	1.608

It appears from this that the viscosity of the sols rises by addition of ammonia, reaches a maximum, and then descends.

3. The great change of viscosity by an added substance in so small a concentration as is the case with the acids, certainly makes the impression of an electro-viscous effect.

In fig. 2 a graphic representation is given of the results of all examined electrolytes, but only for concentrations below 6 mMol per litre. We have always taken the relative viscosity of the electrolyte-

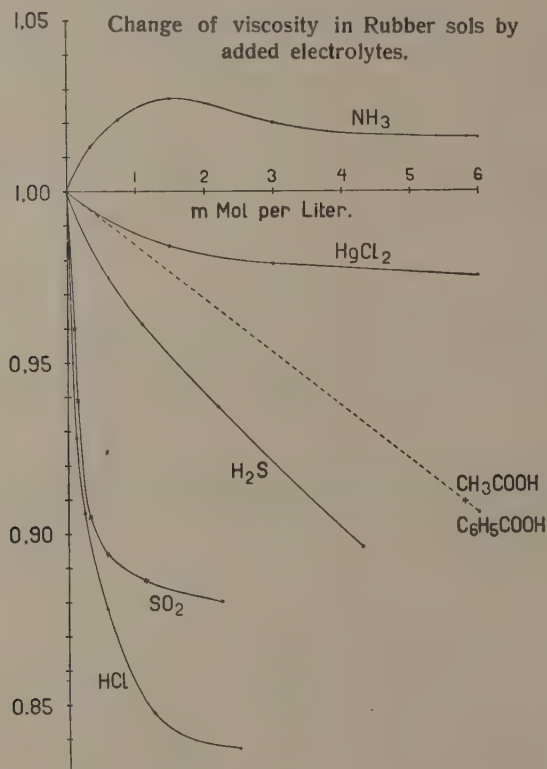


Fig. 2.

free sol as unit, and then plotted the relation  $\frac{\eta_{s+e}-1}{\eta_s-1}$  as ordinates.

The behaviour of NH<sub>3</sub> is in striking agreement with this explanation: for it has appeared in all investigations on capillary-electric phenomena that alcaleic substances give a higher potential to a negatively charged wall, lowering it again on further addition<sup>1)</sup>. In harmony with this researches in this laboratory by Mr. LIER confirmed the occurrence of an increasing electro-viscosity by hydroxyl

<sup>1)</sup> See e.g. G. VON ELISSAFFOF, Z. physik. Chem. **79**, 385 (1912); R. ELLIS, Z. physik. Chem. **80**, 597 (1912); H. R. KRUYT and A. E. VAN ARKEL, Koll. Z. **32**, 29 (1923).



ions in casein, those by Dr. RUNGENBERG DE JONG did so in amylum<sup>1)</sup>. Especially this positive effect is, therefore, a forcible argument in favour of our view.

4. Two objections may, however, be raised. The first is: is  $\text{NH}_3$  and also is  $\text{SO}_2$  in benzene an electrolyte? For the formation of an OH-ion from  $\text{NH}_4\text{OH}$ , resp. an H-ion from  $\text{H}_2\text{SO}_4$ , the presence of water is required. If it is, however, calculated how much water is required with the very small concentrations in question, values are found which are only a small part of the solubility of water in benzene, a quantity that is certainly always present in benzene that has not been dried with particular precautions.

A second objection might be supplied by the question whether the electrolytes in benzene are sufficiently dissociated to put these phenomena to their account. WALDEN's<sup>2)</sup> investigations, however, may reassure us in this respect. Equal dissociation in two solvents is attained at dilutions that are to each other as the third powers of the dielectricity constants, i.e. for the relation benzene-water  $4,7 \times 10^4$ . Hence the succession of the strengths is the same in two solvents. If now according to WALDEN the  $\alpha$  is calculated for HCl in benzene, conc. 1 mMol per litre, taking into account that the constant from OSTWALD's law of dilution varies proportional to the concentration of the undissociated molecules, the value  $\alpha=0,32$  is found. Here there is, therefore, a considerable ionisation. With a weak acid, as benzoic acid, the dissociation is, indeed, more greatly lowered by benzene than in the case that the substance is dissolved in water, but in the concentrations in question here, it is yet not less than  $1/200$  of that in water.

There is, however, a striking difference between the electro-viscous phenomena in water and those in benzene. In water the curves for cations of equal valency coincide, but this is not the case for our curves, though they all have the H-ion as discharging ion (with the exception of  $\text{HgCl}_2$ ). It makes the impression that the real H-ion concentration plays a part: for the anorganic acids discharge in the order of their strength. The two organic acids are, indeed, stronger than  $\text{H}_2\text{S}$ , but organic anions always counteract the discharge through their greater absorbability, the aromatic ion more strongly than the aliphatic one, thus compensating its greater strength. The exceedingly

<sup>1)</sup> Still unpublished; compare however for casein W. PAULI, *Kolloidchemie der Eiweisskörper*, 81 et seq. (Dresden-Leipzig 1920) and for amylum M. SAMEC *Koll. Beih.* **4**, 132 (1913), **5**, 141 (1914) etc.

<sup>2)</sup> P. WALDEN, *Z. physik. Chem.* **94**, 363 (1920).

weakly ionized  $\text{HgCl}_2$ , has accordingly the smallest discharging power.

5. In conclusion we wish to draw attention to a consequence of the stated electro-viscous character of part of the viscosity in the rubbersol. It has often been tried to compare the quality of different samples of rubber by measuring the viscosity of benzene solutions of the same concentration. The choice of this property for a comparison is not unlogical, as in the first instance the viscosity may be considered as a measure for the solvation, and this can be taken into account as a real colloid characteristic. Experience now actually teaches that there exists a certain correlation between the viscosity of the sol and the mechanic properties which determine the quality; it is, however, no more than a vague correlation. It has, however, appeared above, that part of the viscosity is *not* in connection with the solvation, but is of electric origin, and has, therefore, a perfectly casual character, dependent on the soluble components which accompany the rubber and which have no influence on the mechanic properties in these minimum concentrations. If it is, therefore, desired to detect a functional relation between viscosity and the properties of the quality of the rubber, it will be necessary to eliminate beforehand the electro-viscous effect by judicious addition of the electrolyte.

We consider the knowledge of these electro-viscous phenomena of importance from the standpoint of pure colloid chemistry, because they open a way to the study of the electric relations in non-aqueous sols.

*Utrecht, VAN 'T HOFF-laboratory, 1922.*

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**Physics.** — *“Isotherms of di-atomic substances and their binary mixtures. XX. The critical curve of oxygen-nitrogen mixtures, the critical phenomena and some isotherms of two mixtures with 50% and 75% by volume of oxygen in the neighbourhood of the critical point.”* By J. P. KUENEN †, T. VERSCHOYLE and A. TH. VAN URK. Communication No. 161 from the Physical Laboratory at Leiden. (Dr. KAMERLINGH ONNES, holding his deeply regretted friend in affectionate memory, is glad to perform the honourable task of presenting for the Proceedings a paper by the late Dr. KUENEN which was made almost ready for the press),

(Communicated at the meeting of November 25th, 1922).

### § 1. *Introduction.*

This work is a continuation of that of KUENEN and CLARK<sup>1)</sup>, the investigations, however, being carried out in such a way as to allow of the construction of complete isotherms, which involved a slight modification of the apparatus then used. The mixtures on which measurements were made, contained respectively 50% and 75% by volume of oxygen, and it was found that these gave sufficient data for the construction of the critical curve. This was found to be almost a straight line, while both critical constants proved to be an almost linear function of the composition.

### § 2. *Preparation of the mixtures.*

A simple mixing apparatus was employed, consisting essentially of a measuring-bulb of about a litre capacity, surrounded by a water-jacket and connected with an open manometer tube, in which the gases to be mixed were measured, and of a mixing bulb of some 2 litres capacity. Through 3-way taps the bulbs could be put in connection with each other, the source of gas, the piezometer to be filled, and a vacuum pump, as might be desired. In measuring the relative quantities of the gases to be mixed, the mercury was

<sup>1)</sup> J. P. KUENEN and A. L. CLARK. These Proc. XIX (2) pg. 1088. (Febr. 1917.) Leiden Comm. N°. 150b.

always brought to a mark on the stem below the measuring-bulb, when the pressure-difference was read with a cathetometer, allowing for the height of the barometer, while the temperature of the waterjacket was observed.

The oxygen was prepared from pure potassium permanganate<sup>1)</sup> and the nitrogen from solutions of sodium nitrite and ammonium chloride<sup>1)</sup>. In the preparation of nitrogen the air was first driven out by carbon dioxide; to free the nitrogen from the remaining carbon it was frozen out in liquid oxygen boiling under reduced pressure, before being used. The first part of the evaporating nitrogen was pumped off, and the next part used to fill the apparatus; the residue was also removed.

### § 3. Apparatus.

#### *a. Piezometer.*

The usual type of piezometer used in the laboratory at Leiden was employed. The volume of the large reservoir was some 500 cm<sup>3</sup>. and that of the small reservoir about 1 cm<sup>3</sup>. The form of the latter differed from that used in Comm. N°. 150*b* as an other method of stirring was adopted, to avoid the difficulties mentioned there. It consisted of a capillary about 50 cm. long *C*, with a bore of  $\pm 0.2$  mm., and a cylindrical bulb *R*, about 10 cm. long, which was carefully rounded at the lower end, so that the stirrer *r* contained within (a short length of iron wire enclosed in a glass tube) could reach the extreme end, thus avoiding any dead space. The bulb *R* was graduated; and, as its section and the volume of the stirrer were known by previous calibration, it was possible to estimate the volume of any liquid formed in it. The reservoir was calibrated as a whole after its construction had been completely finished.

#### *b. Manometer.*

Pressures were read on the closed hydrogen manometer M. 60<sup>1)</sup>. For the arrangement of the pressure connections and of the piezometer, reference may be made to Comm. N°. 97*a*. (Plate I.)

#### *c. Cryostat.*

The cryostat contained, besides the small reservoir *R* two platinum resistance thermometers *W* for reading the temperature, a stirrer *B* for the cryostat liquid (in this case ethylene), and the usual auxiliary

<sup>1)</sup> H. KAMERLINGH ONNES, G. DORSMAN and G. HOLST. Proc. XVII (2) pg. 950. (Dec. 1904). Leiden. Comm. N°. 145*b*.

<sup>2)</sup> These Proc. IX p. 754 (Dec. 1906). Leiden Comm. N°. 97*a*.



capillary *H*, a simple helium thermometer<sup>1)</sup> for ascertaining the mean temperature of the portion of the small reservoir capillary within the cryostat, but above the liquid, as well as the necessary tubes for the introduction and removal of the ethylene.

The connections, required for the regulation of the pressure within the cryostat may be seen in Plate I of Comm. N°. 97<sup>a</sup>.

The method of stirring the gaseous and liquid phases within the small reservoir bulb was as follows: round the bulb was fitted a soft iron sheath, which could be moved vertically up and down by means of an electro-magnet *E* above the cryostat, in the same way as the liquid stirrer is worked.<sup>2)</sup> In the lowest position of the sheath *m* (which is of about the same length as the reservoir *R*, and about three times as long as the stirrer), the lower edge was at the level of the bottom of the bulb *R*; in the highest position of *m* its lower edge was raised to fully two thirds of the height of the bulb *R*. In order to be able to obtain a clear view of the whole length of the bulb *R*, two slits were cut out of opposite sides of the sheath *m*, and the latter so arranged that these slits were in line with the clear strips in the silver surfaces of the vacuum-glasses. Round the outer glass a ring electro-magnet *m* was placed with the bottom surfaces slightly above the level of the top of the bulb *R*. By a correct adjustment of the current circulating through this and the weight of the iron sheath *m*, it was possible to raise and lower the latter, which carried the small stirrer *r* with



Fig. 1.

<sup>1)</sup> These Proc. IX pg. 754. (Dec. 1906). Leiden Comm. N°. 97<sup>a</sup>.

<sup>2)</sup> These Proc. XX (2) pg. 991 (June 1917). Leiden Comm. No. 152<sup>a</sup> (§ 3).

it, so that the gas and liquid phases in the bulb could be stirred as required.<sup>1)</sup>

#### § 4. *Observations and precautions.*

Before commencing the work at low temperatures, isotherms were experimentally determined for the two mixtures at 20°, the calculations being carried out on the lines of Comm. N°. 78. The values of the expansion coefficients for the mixtures

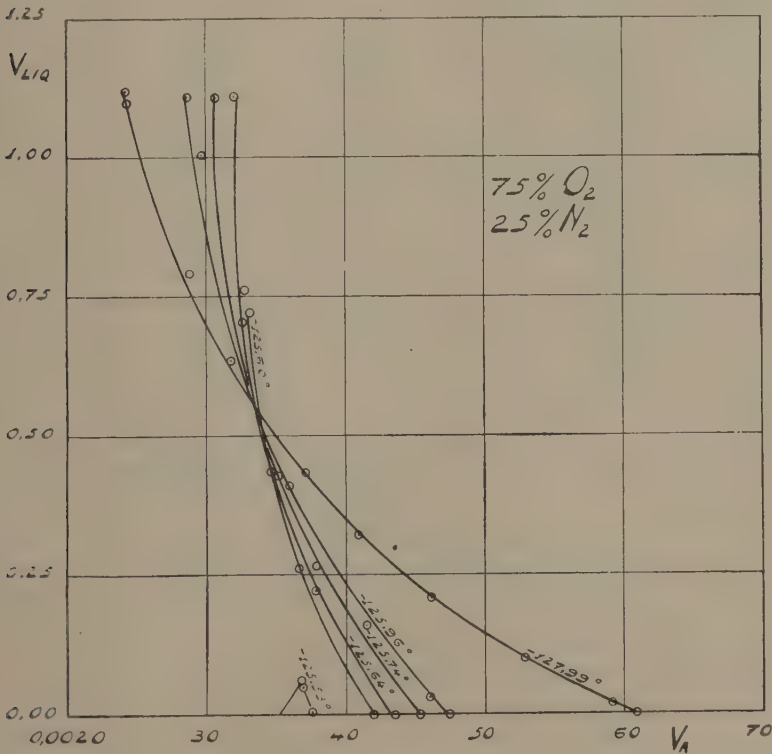
$$\alpha = \frac{1}{v_A} \left[ \left( \frac{\partial v_A}{\partial t} \right)_p \right]_0^{20}$$

required in the calculation of the isotherms were interpolated as linear functions of the composition from the corresponding values of the pure gases, the error involved being negligible. These values were, in the case of oxygen, those found by KAMERLINGH ONNES and HYNDMAN<sup>2)</sup> and, in the case of nitrogen, calculated from isotherms determined at 0° and 20° by one of us, which are not yet published. These normal temperature isotherms were determined with small reservoirs  $\pm 5$  cm<sup>3</sup> volume. For greater certainty a second series of points were determined for the 75% oxygen mixture using the small reservoir of  $\pm 1$  cm<sup>3</sup> of the piezometer used in the critical zone as a leak occurred during the first series, and consequently only the normal volume determined at the end could be used in the calculations. The agreement of this control is satisfactory. Isotherms were made over a range starting about 5 degrees above the temperature of the critical point of contact, and extending as low as the proportions of the piezometer allowed, i.e., 6 degrees below that temperature for the 50% mixture, and  $2\frac{1}{2}$  degrees for the 75% mixture. The temperature intervals were in general some 2 degrees, but, in the neighbourhood of the zone, were reduced to  $\frac{1}{10}$  degree or less. All observations were made with rising pressure, the importance of which fact is insisted on in Comm. 150b; and, after finishing any series, the pressure is completely released, and gas in the piezometer well mixed by successively raising the pressure to 10 atmospheres or so and lowering, before proceeding to a new series. When only one phase was present, the pressure steps were of the order 2—3 atmospheres, but, when two were present, and near the critical zone, they were reduced to a few tenths of an atmosphere and sometimes the raising was accomplished by even

<sup>1)</sup> A. VAN ELDIK. Amsterdam Akad. Versl. Mei—Juni 1897. Leiden Comm. N°. 39.

<sup>2)</sup> These Proc. IV pg. 761. (Maart 1902). Leiden Comm. N°. 78.

smaller steps. As soon as two phases are present, the equilibrium becomes extremely sensitive to the smallest change in pressure or temperature, and therefore the quantities that determine the conditions of equilibrium must be kept as constant as possible. In the critical zone, an alteration of a hundredth of a degree in the temperature will cause the mercury in the stem of the piezometer to rise or fall by millimeters. Although the *end*-points of condensation could be fairly accurately observed, provided the pressure-increases were made with extreme care the tendency of the liquid phase to remain out, despite vigorous stirring, did not allow of accurate observation



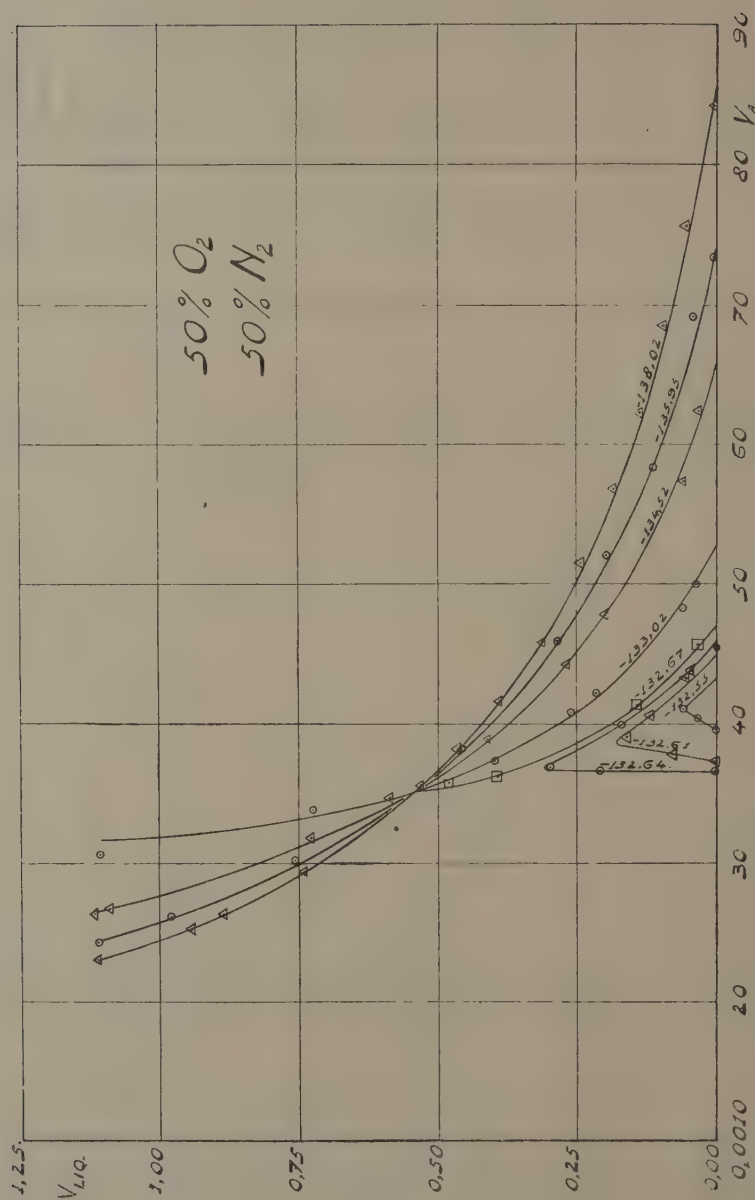


Fig. 3.



retrograde condensation, although the latter was limited to a range of 0.13 degree at most.

As an illustration of the perfection to which the regulation of pressure and temperature has been brought in the Leiden Laboratory, the 50% mixture was maintained under the plait-point conditions for over an hour, the blue opalescence being continually there, while an indefinite meniscus alternately appeared and disappeared in the middle of the bulb on stirring. From the results a  $p, v_A$  graph for each mixture is constructed, and the points of beginning and end condensation determined as previously stated: the border curve is drawn through these. It was found that the two-phase line during the period of observation is to all intents and purposes a straight line, although, in the case of the 50% mixture, the first points determined after condensation lie below this line on every isotherm. This can hardly be explained by any delay in the appearance of the liquid phase (which would give the reverse effect), and the deviation is far greater than any error of observation.

The accuracy of the pressure determination is at least 1 in 5000<sup>1)</sup>; that of the temperature reading within 0.02 of a degree, while the probable observation error of the volumes is not greater than 1 in 2000 when one phase was present, and 1 in 200 when two phases were present — apart from a possible constant calibration error of 1 in 500. To eliminate the last error it would have been necessary to measure a few points of the isotherm of 20° C. of hydrogen with this piezometer, and to compare the results with the accurate isotherm of SCHALKWYK. But as such accuracy was of little importance in our case, this was not done.

The results for the two mixtures are given below with:

$p$  = pressure in atmospheres.

$v_A$  = volume, expressed in the normal volume.

$V_L$  = volume of liquid, expressed in volume of the small reservoir.

$\theta$  = temperature on the provisional intern. Kelvin scale, reduced by 273.09.

The condensation points, as found from the  $p, v_A$  graphs, are plotted on a  $p, t$  ( $t = \theta$ ) graph; the results of KUENEN and CLARK being included on the same graph. (Fig. 4). The vapour pressures of pure oxygen<sup>2)</sup> and nitrogen<sup>3)</sup> are also plotted, and the critical

<sup>1)</sup> C. A. CROMMELIN and Mej. E. J. SMID. These Proc. XVIII (1) pg. 472. Leiden. Comm. Leiden. N°. 146c.

<sup>2)</sup> H. KAMERLINGH ONNES, C. DORSMAN and G. HOLST, l. c.

<sup>3)</sup> C. A. CROMMELIN. These Proc. XVII (2) 959 (Dec. 1914.) Leiden Comm. N°. 145d.

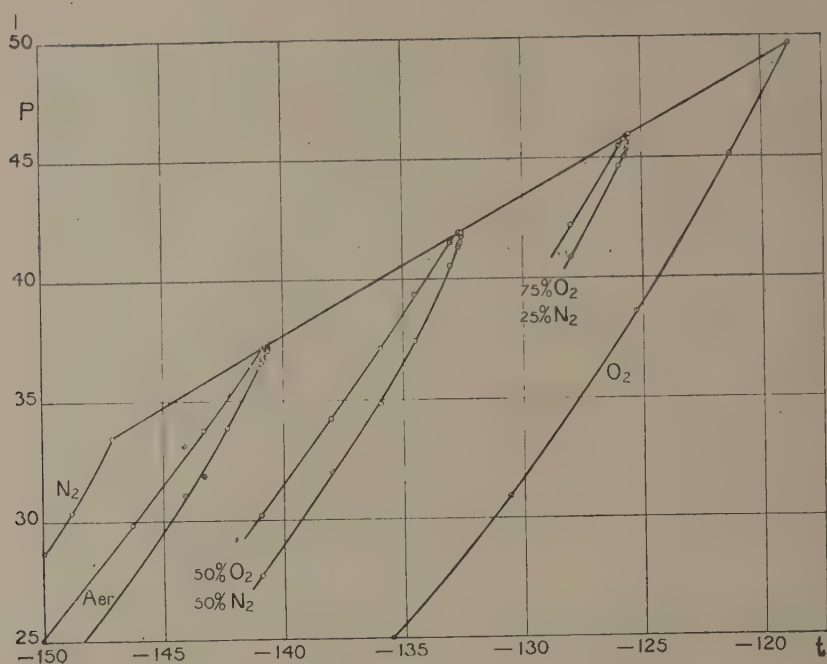


Fig. 4.

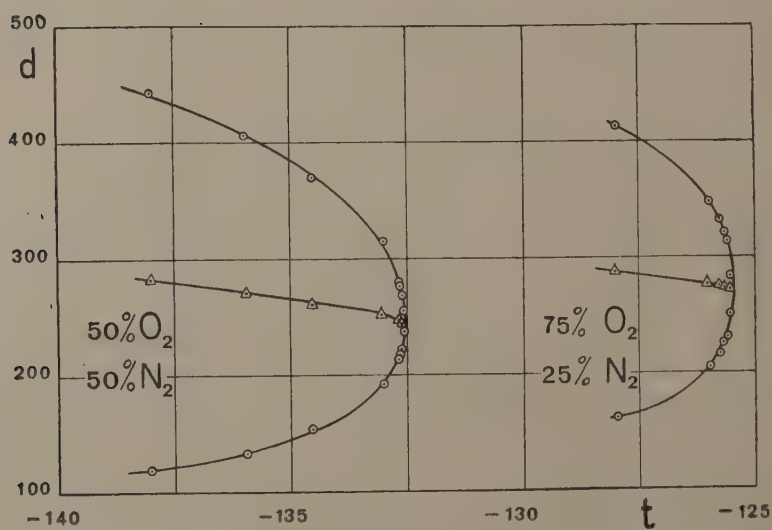


Fig. 5.

curve drawn tangential to the various border curves, touching those in the plait points.

By plotting  $V_L$  the volume of the liquid against  $v_A$  a series of curves are obtained which clearly show the process of retrograde condensation in the case of the 50% mixture<sup>1)</sup>.

A peculiarity of the last mixture is that all the lines in this graph go through the point  $V_L = \text{half the volume of the small reservoir}$ , which means that the corresponding line of constant division of volume is a line of constant  $v_A$ , therefore in the  $p, v_A$  diagram it runs parallel to the  $p$ -axis<sup>2)</sup>.

If a  $d_A, t$  graph is drawn, a diameter is obtained which is rectilinear (as for a pure substance), but which is strongly curved towards the temperature axis at the extreme end, though in this zone, the position of the point as found must be necessarily rather qualitative than quantitative.

The plait-point constants were found to be:

50% $O_2$ Mixture. (series XIV. 4.)		75% $O_2$ Mixture. (series IX. 5.)	
$p$	41.90	45.89	(observed)
$v_A$	0.00358	0.00336	(from $p, v_A$ graph)
$\theta$	$-132^\circ.66$	$-125^\circ.60$	(observed)

The critical point of contact constants were found to be:

(series IX. 4.)		(series X. 3.)	
$p$	41.90	45.86	(from $p, v_A$ graph)
$v_A$	0.00404	0.00375	(from $d_A, t$ graph)
$\theta$	$-132^\circ.53$	$-125^\circ.53$	(observed)

For the critical point of contact temperature it was found that, at 0.01 of a degree above it no condensation was, of course, observed, and at 0.01 below there was a momentary, but very evident condensation.

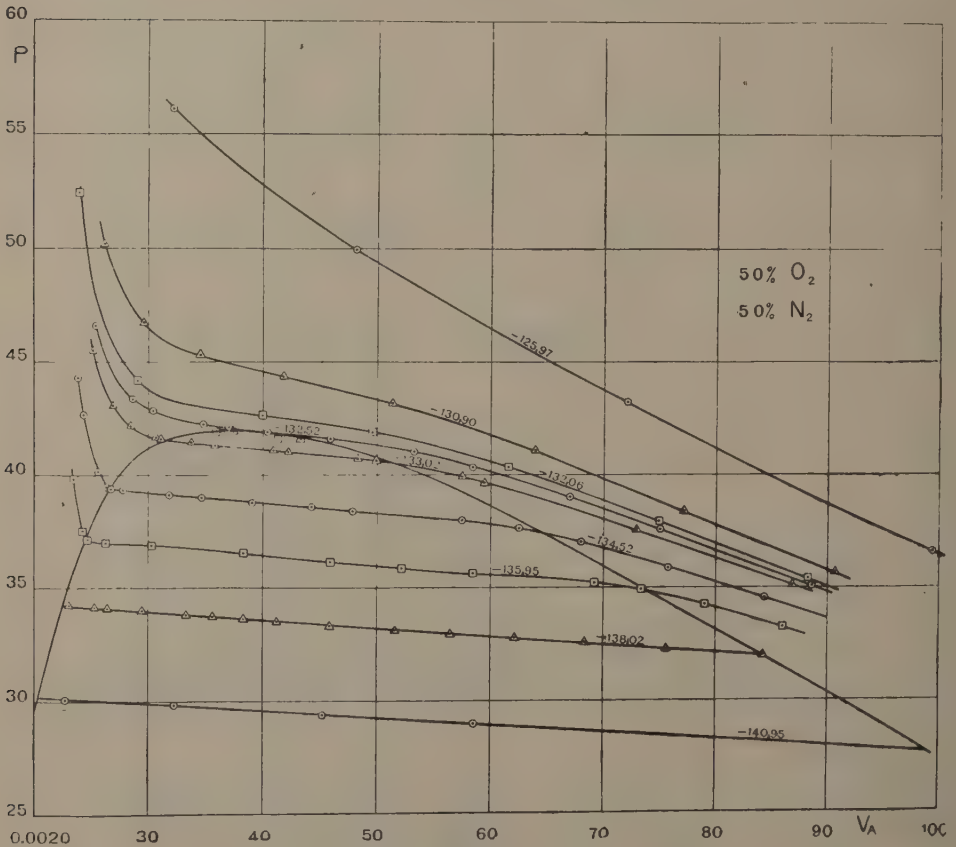
<sup>1)</sup> J. E. VERSCHAFFELT. These Proc. I. pg. 288 (Dec. 1898.) Leiden Comm. N<sup>o</sup>. 45.

<sup>2)</sup> Leiden Comm. Suppl. N<sup>o</sup>. 23, p. 51. Enc. Math. Wiss. V 10.

Results for the mixture 50 %  $O_2$ —50 %  $N_2$ .

*Isotherm of 20° C.*

Point.	$p$	$d_A$	$pv_A$	Point.	$p$	$d_A$	$pv_A$
1	34.24	32.39	1.0573	7	52.34	49.82	1.0507
2	37.55	35.56	1.0561	8	46.25	43.91	1.0533
3	41.39	39.25	1.0548	9	41.12	38.99	1.0546
4	46.41	44.07	1.0531	10	37.28	35.28	1.0567
5	51.88	49.37	1.0508	11	34.03	32.17	1.0579
6	51.85	49.35	1.0507				





*Isotherms at low temperature.*

Point	$p$	$v_A$	$V_L$	$\theta$	Point	$p$	$v_A$	$V_L$	$\theta$
I. 1	37.12	0.01080		-120°.76	IV. 1	35.41	0.00882		-132°.06
2	44.81	00793		8	2	37.95	749		6
3	54.30	533		6	3	40.33	615		6
II. 1	36.57	0.00994		-125°.97	4	41.91	495		7
2	43.23	721		7	5	42.67	398		6
3	49.95	481		8	6	44.17	290		6
4	56.13	322		7	7	52.44	239		6
III. 1	35.65	0.00907		-130°.90	IX. 1	35.08	0.00886		-132°.51
2	38.38	771		0	2	37.57	751		1
3	41.03	639		89	XV. 1	39.03	670		2
4	43.16	513		91	IX. 3	40.34	584		1
5	44.35	418		0	XV. 2	41.02	532		2
6	45.26	345		0	3	41.60	458		2
7	46.73	295		0	IX. 4	41.90	404		3
8	50.18	261		0	5	42.13	369		0
					XV. 4	42.25	347		2
					5	42.78	303		2
					IX. 6	43.38	285		1
					XV. 6	46.60	253		2

Point	$p$	$v_A$	$V_L$	$\theta$	Point	$p$	$v_A$	$V_L$	$\theta$
X. 1	41.84	0.00410	0.051	-132° .56	VI. 4	41.69	0.00306	1.000	-132° .00
2	41.89	403	029	5	V. 6	42.16	284		3
3	41.93	395	000	5	XVI. 6	43.13	268		1
					7	45.78	251		2
XII. 1	41.60	0.00436	0.042	-132° .61					
XI. 1	41.62	433	046	0	XVII. 1	34.52	0.00843		-134° .50
XII. 2	41.77	406	107	0	2	35.89	757		2
XI. 2	41.85	392	138	1	3	37.03	680		1
XII. 3	41.92	379	068	0	4	37.60	624	0.030	1
XI. 3	41.95	372	000	1	5	37.98	574	054	3
XII. 4	41.97	373	000	0	6	38.41	478	177	2
					7	38.58	442	240	2
XIII. 1	41.46	0.00455	0.000	-132° .64	8	38.80	390	369	2
2	41.75	399	151	4	9	39.01	346	524	2
3	41.89	369	268	4	10	39.14	318	653	1
4	41.91	366	186	4	11	39.33	277	916	2
5	41.91	366	000	4	12	39.40	267	978	3
					13	39.46	263	1.000	2
XIV. 1	41.40	0.00455	0.026	-132° .67	14	40.15	256		1
2	41.61	413	123	7	15	42.64	242		2
3	41.89	362	350	7	16	44.25	237		2
4	41.90	358	430	6					
V. 1	35.12	0.00867		-133° .01	XVIII. 1	33.21	0.00860		-135° .98
2	37.58	728		1	VII. 1	34.32	790		1
3	39.67	594		3	XVIII. 2	34.85	733	0.002	8
XVI. 1	39.92	574		3	VII. 2	35.21	692	037	1
VI. 1	40.62	499	0.031	2	3	35.66	584	101	3
XVI. 2	40.65	527		2	XVIII. 3	35.82	521	175	7
V. 4	40.73	482	54	1	4	36.14	459	255	7
VI. 2	41.03	421	192	0	VII. 4	36.60	382	408	1
XVI. 3	41.08	408	235	2	XVIII. 5	36.90	302	677	7
VI. 3	41.29	373	356	-132 .99	6	37.09	262	877	6
V. 5	41.34	358	472	-133° .03	VII. 5	37.19	246	990	2
XVI. 4	41.46	336	648	2	6	37.56	242	1.000	2
5	41.62	310		2	XVIII. 7	39.77	234		7

Point	$p$	$v_A$	$V_L$	$\theta$
XIX. 1	32.02	0.00842	0.000	$-138^\circ.02$
2	32.31	755	048	2
3	32.57	684	082	2
4	32.78	621	123	2
5	32.98	564	165	2
6	33.16	514	219	1
7	33.37	457	279	2
8	33.54	415	349	2
9	33.65	382	414	2
10	33.75	355	480	2
11	33.84	331	540	2
12	33.99	293	663	1
13	34.11	263	792	1
14	34.16	253	843	1
15	34.24	230	1.000	2
VIII. 1	27.69		0.000	$-140^\circ.95$
2	28.99	0.00585	186	5
3	29.41	452	316	5
4	29.85	322	544	4
5	30.09	227	901	6

Results for the mixture 75 %  $O_2$ —25 % N.

*Isotherm of 20° C.*

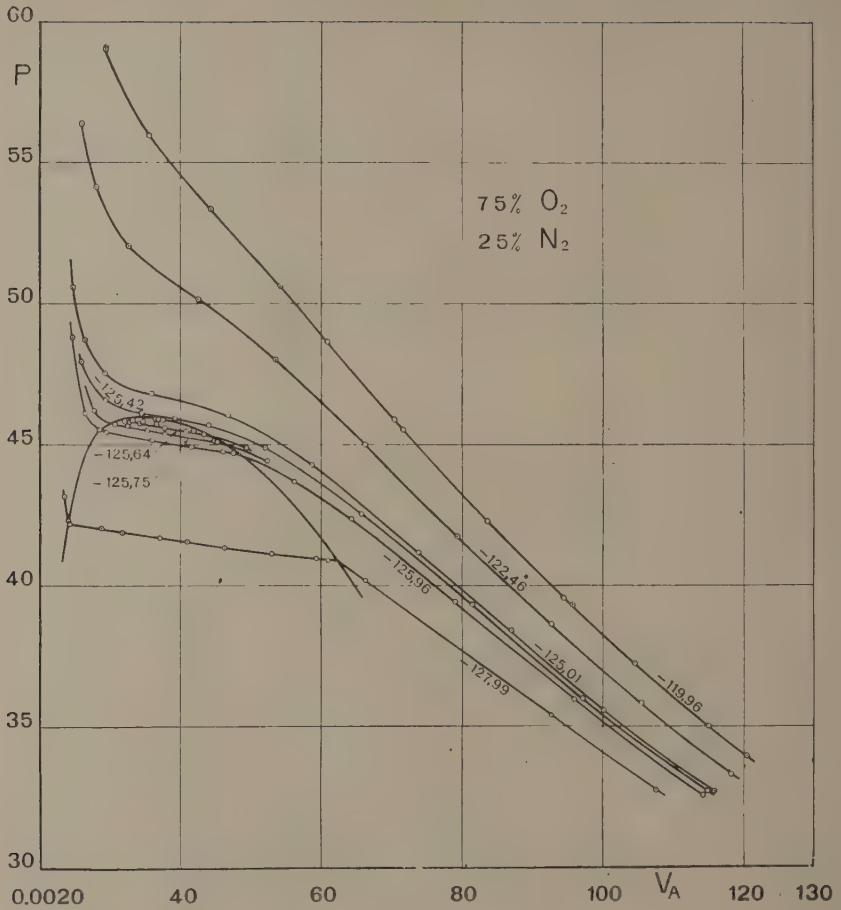
Point	$p$	$d_A$	$pv_A$	Point	$p$	$d_A$	$pv_A$
I. 1	51.68	49.49	1.0441	II. 1	36.91	35.08	1.0521
2	45.18	43.15	1.0471	2	42.90	40.89	1.0492
3	40.12	38.20	1.0503	3	48.79	46.63	1.0464
4	35.91	34.14	1.0520	4	56.40	54.08	1.0429
5	32.69	31.01	1.0542				
6	28.89	27.34	1.0564				

*Isotherms at low temperature.*

Point	$p$	$v_A$	$V_L$	$\theta$	Point	$p$	$v_A$	$V_L$	$\theta$
I. 1	33.93	0.01206		-119°.95	II. 7	50.16	0.00426		-122°.47
7	35.00	1151		7	8	52.05	327		6
2	37.20	1045		5	9	54.15	280		6
3	39.31	0956		5	10	56.41	260		6
8	39.55	944		6	III. 1	32.71	0.01159		-125°.00
4	42.27	835		5		2	35.59	1006	0
5	45.54	715		4		3	38.40	0869	4.99
9	45.88	704		6		4	41.19	737	5.01
6	48.66	608		4		5	44.28	587	1
10	50.64	540		7		6	46.04	467	1
11	53.36	443		8		7	46.83	359	1
12	55.97	355		6		8	47.51	293	1
13	59.13	294		7		9	48.73	265	1
						10	50.60	248	2
II. 1	33.29	0.01183		-122°.47					
2	35.82	1055		6					
3	38.60	0926		6					
4	41.72	793		6					
5	45.00	661		7					
6	48.02	535		6					



Point	$p$	$v_A$	$V_L$	$\theta$	Point	$p$	$v_A$	$V_L$	$\theta$
VI. 1	32.68	0.01149		-125°.42	VII. 6	45.65	0.00326	0.631	-125°.73
2	35.97	9973		3	7	45.70	307	1.000	4
3	39.30	813		2	8	46.19	277		3
4	42.54	657		2					
5	44.89	520		1	IV. 1	32.53	0.01143		-125°.96
6	45.67	440		2	2	35.93	0959		6
7	45.93	382		2	3	39.41	789		8
8	46.14	346		3	4	42.37	641		7
9	46.59	294		2	5	43.68	561		7
10	47.95	261		2	6	44.67	474	0.000	7
					7	44.75	460	025	6
					8	44.91	415	142	6
X. 1	45.89	0.00369	0.041	-125°.53	9	45.15	361	368	6
2	45.90	345	53	3	10	45.43	297	901	6
3	45.86	375	000	3	11	45.51	287	1.000	6
					12	46.11	267		6
					13	48.83	248		6
IX. 1	45.49	0.00419	0.000	-125°.60					
2	45.72	366	236	0	V. 1	32.74	0.01076		-127°.99
3	45.81	347	394	0	2	35.41	0926		8.00
4	45.85	333	648	59	3	38.10	785		0
5	45.89	336	1.000	60	4	40.19	663		0
					5	40.89	609	0.000	7.99
VIII. 1	44.89	0.00394		-125°.64	6	40.95	592	020	9
2	45.36	433	0.000	4	7	41.14	529	090	9
3	45.46	408	78	4	8	41.38	462	186	9
4	45.59	378	199	3	9	41.55	409	289	9
5	45.75	343	455	4	10	41.70	371	389	8.00
6	45.80	328	682	4	11	41.88	318	569	0
7	45.83	321	1.000	5	12	42.04	288	709	7.98
					13	42.19	244	994	9
VII. 1	44.43	0.00523		-125°.75	14	42.28	242	1.000	9
2	45.09	453		5	15	43.17	236		8.00
3	45.12	448	0.000	4					
4	45.38	378	239	6					
5	45.50	354	384	4					



In conclusion it is our pleasant duty to thank Miss H. VAN DER HORST and Mr. J. D. A. Boks for their careful regulation of the temperature, and Mr. L. OUWERKERK and Mr. C. F. L. KRAANEVELD for the technical skill with which they helped us during the whole course of the measurements.

**Anatomy.** — “Contributions to the knowledge of the brain of bony fishes.” By Prof. KYOZO KUDO, Mukden (Manchuria). (Communicated by Dr. C. U. ARIËNS KAPPERS).

(Communicated at the meeting of January 27, 1923).

### I. *The Tr. olfactorio-opticus.*

NILS HOLMGREN found in *Osmerus eperlanus* with the CAJAL-method, but also with methylene-blue colouring, a bundle which, long before the middle of the telencephalon, separates from the tr. olfactorius lateralis, then, following the sulcus externus, extends as far as the opticus, into which it enters, and can be traced (in the opticus) for some distance towards the eye. He called the bundle *tr. olfactorius lat. optici* (op. cit., p. 188). With *Callionymus lyra* he found a similar bundle, but lying in the medial olfactory tract (i.e., p. 188, Anmerkung).

This discovery should be considered most remarkable. Being able to test and confirm the latter case (the fibres in the tr. olfactorius med.) with various Teleosts also by WEIGERT-preparations, I will describe it here more fully.

With the WEIGERT-colouring these fibres, connecting the tr. olfactorius with the tr. opticus, seem fairly coarse; they are nearly always scattered and mixed only with the tr. olfactorius medialis, never with tr. olfactorius lateralis. In the bony fishes, which I examined they run always the same way. As these relations are the most distinct in *Ammodytes tobianus*, I take this fish as example.

With this fish the tr. olfactorius med. consists of two sorts of medullary fibres, a thin one and a much coarser one. The fibres divide into three parts.

The *pars dorsalis* is that part of the tr. olfactorius med. that on a quite frontal level turns towards dorsal. It consists for the greater part of thin fibres that radiate in dorso-lateral direction and disappear rather soon, already on the level of commissura anterior. A few coarse fibres, however, also belonging to this portion, run further caudad, always following laterally the tr. olfacto-hypothalamicus med., but strongly contrasting with these by their coarseness. They cannot be traced accurately from the place where they medially

pass the *fibrae ansulatae* of BELLONCI, caudo-ventrally descending by and by with the accompanying *tractus olf.-hypothal. med.*

These fibres form the *dorsal* group of the coarse olfactory fibres.

The *pars intermedia* of the *tr. olfact. med.* consists half of the thinner, and half of the coarser fibres. The first form a small bundle and cross in the commissura anterior (the so-called *comm. interbulbaris*).

The *pars ventralis* is formed by coarse fibres exclusively. They at first join to a bundle, but gradually they separate into several small bundles. These, together with the fibres from the *pars intermedia* form the *ventral* group of the coarse olfactory fibres. The bundles soon arrange in regular order dorso-ventrally in the *praethalamus*, thereby dorsally touching the *tr. olfacto-hypothalamicus med.*, ventrally the *tr. opticus*, into which they are taken up gradually (fig. 1). A few fibres that are in an exceptional dorsal position, enter into the just rising *commissura minor*.

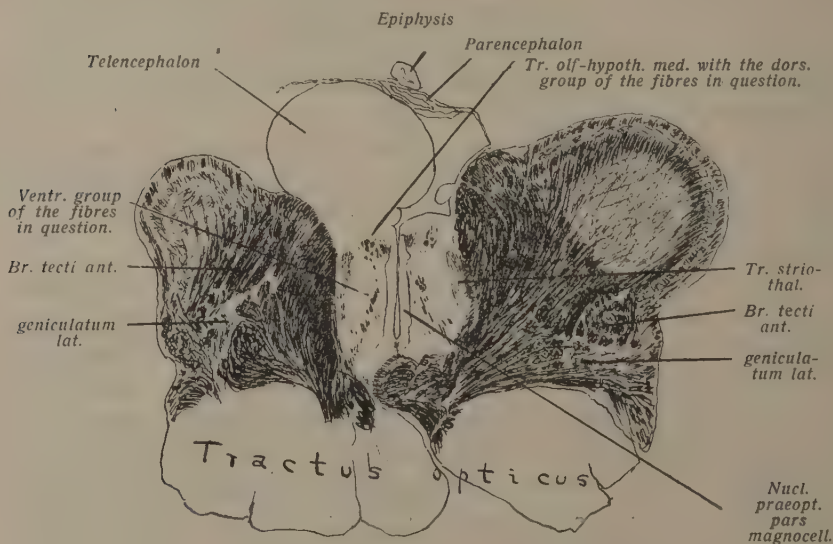


Fig. 1. *Ammodytes tobianus*.

(Preparation of the Central Institute for Brain-research, Amsterdam).

With other bony fishes the course of these coarse olfactory fibres is nearly the same. Only the relation to the *commissura minor* (and to the *fasciculus medialis n. optici*) does not always exist, this being most distinct, besides in *Ammodytes*, with *Rhombus*, *Hippocampus* and *Morone*.

I have been able to find these fibres with *Catostomi*, *Percesoces*,



Acanthopterygii and Plectognathi, but not with Malacopterygii, Ostariophysi, Symbranchii and Haplomi. They probably are neither to be found with Anacanthini and Pediculati (at least not medullated).

The quantity of the fibres varies according to the kind of fishes. It often is so small that the fibres can be easily counted. In any case the fibres are generally not very numerous. The *ventral* group is always superior in number to the *dorsal*, which I even cannot find in *Solea* and *Cottus*.

With *Callionymus lyra*, the very bony fish that HOLMGREN examined, the matter is somewhat different.

Insofar as it may be judged by WEIGERT-PAL series these fishes show no tr. olfactorius lat. The tr. olfactorius med. is fairly coarse and is found as usual on the medio-ventral side of the frontal half of the brain. Caudally it soon descends a little ventrally already before the level of the commissura minor, and comes in touch with the opticus fibres and especially with those that arrive here from lateral. I think it fairly probable that fibres are being exchanged between these two tracts, that is to say that tr. olfactorius gives away a part of its fibres to the tr. opticus, but in exchange receives more fibres from the latter tract during its descension (see below) and so becomes visibly coarser. The fibre tract now runs medially along the dorsal opticus root in a ventral direction.<sup>1)</sup> More frontal a small part of the tr. olfactorius is separated from the chief bundle on the spot where this tract begins to descend in order to come into touch with the tr. opticus. This separated little bundle runs independently in the praethalamus also ventrad, about in the middle of the inner and outer surface of same, and finally joins again the principal bundle.<sup>2)</sup>

When the thus formed olfacto-optic bundle has at last left the tr. opticus, it runs lateral, viz. between the tr. strio-thalamicus med. and the nucl. anterior thalami?<sup>3)</sup>. More caudally it wedges between the nucl. praerotundus?<sup>3)</sup> and the tr. tubero-dorsalis of GOLDSTEIN. A little way back nerve cells begin to appear in the bundle and finally take up the area of the bundle nearly entirely. This nucleus takes its place quite superficially of the lateral surface of the hypothalamus, close above the lobus inferior (see fig. 87 of HOLMGREN'S

<sup>1)</sup> The formation of the very extensive tectum plate and accordingly the topography of the opticus roots are in this bony fish different from others.

<sup>2)</sup> So with *Callionymus* nearly all medullary olfactory fibres seem to run as far as into the praethalamus.

<sup>3)</sup> I have not yet succeeded in identifying these nuclei free from objection with this fish.

work, showing the nucleus in question, medial of "tr. olf. tect. sem."). The cells of this nucleus are small.

From this nucleus proceeds a new fibre tract, running in a curve in the torus semicircularis, parallel to and inward of the tr. isthmio-tectalis mihi (see below), yet it seems to end in the torus itself. That besides this, fibres should come from the said tract in the path of the tr. tecto-bulbaris or tr. tecto-isthmicus into the tectum, as HOLMGREN seems to presume, is improbable to me<sup>1)</sup>.

As to the origin and the end of my coarse olfactory fibres, I am quite unable yet to say anything definite. That frontally they are connected with the bulbus olfactorius is undoubtedly sure, but their caudal destination remains quite uncertain. HOLMGREN seems to hold the opinion that his tr. olfactorius lat. optici runs centrifugally in the opticus (l.c., p. 188). I myself am more inclined to believe that the fibres of the *ventral* group tend through the path of the commissura transversa towards the tectum or, less probable, towards the nucl. praerotundus of the other side, the spot where they penetrate into the opticus root just corresponding with the most frontal level of this commissure. This, however, is a mere supposition.

It is harder still to say anything of the *dorsal* group of my fibres.

Concerning the curious olfacto-optic bundle in Callionymus, it can only be said that the part of tr. olfactorius med., that enters frontally into the opticus, corresponds fairly certainly with the *ventral* group of my fibres. But about the other part of the tract, the associating opticus fibres, the peculiar nucleus and the bundle originating from it, I cannot give an opinion, as — till now — I have not seen anything similar with the other bony fishes.

Summarizing we find in the brain of the Teleosts a remarkable fibre system, connecting the tr. olfactorius with the tr. opticus, consisting in the more primitive forms (*Osmerus eperlanus*) of thin fibres (that can only be exposed by the impregnation method) running in the tr. olfactorius lat., whereas in the more highly organised forms it has coarse, medullary fibres as components and is mixed between the fibres of the tr. olfactorius med.<sup>1</sup> At the present I must be content with confirming HOLMGREN's finding, leaving the arising questions to later investigations.

## II. The *Tr. tecto-praerotundus*.

I think I have discovered in the brain of bony fishes a medul-

<sup>1)</sup> HOLMGREN, namely in fig. 87 of his work, has indicated this newly forming fibre tract as „tr. olfacto-tectalis et semicircularis”, without further referring to it in the text.

lary fibre tract, not yet described as far as I know, which probably connects the tectum with the nucleus praerotundus. This tract appears in transverse sections on the level where the fasciculus medialis nervi optici, swinging across the tr. strio-thalamicus, joins the lateral opticus root. It there appears as a bundle, running dorso-ventrally, medially along the dorsal opticus root. Dorsally it lies in separate bundles between the just-mentioned opticus root and those fibres that branch off (more frontally) from the tr. opticus, run dorsad in the post-habenular region and finally lateral into the deep medullary layer tectum. From these fibres (probably corresponding to the *fibræ tectales n. optici* of KRAUSE) the tract is distinguished by the smaller caliber of its fibres and its steeper course. Somewhat more caudally it bends in a lateral direction and enters also into the deep medullary layer of the tectum.

Ventrally it crosses with the fasciculus med. n. optici directly medially to the praetectal nucleus, then runs laterally down from the tr. strio-thalamicus, to finally join the fibres of the commissura transversa (see fig. 2).

Often, however, it does not run laterally to the tr. strio-thalamicus but medially, together with the fasciculus med. n. optici towards medioventral, consequently in this case delusive of a commissura minor in the sense of ARIËNS KAPPERS (one-sided in a specimen of

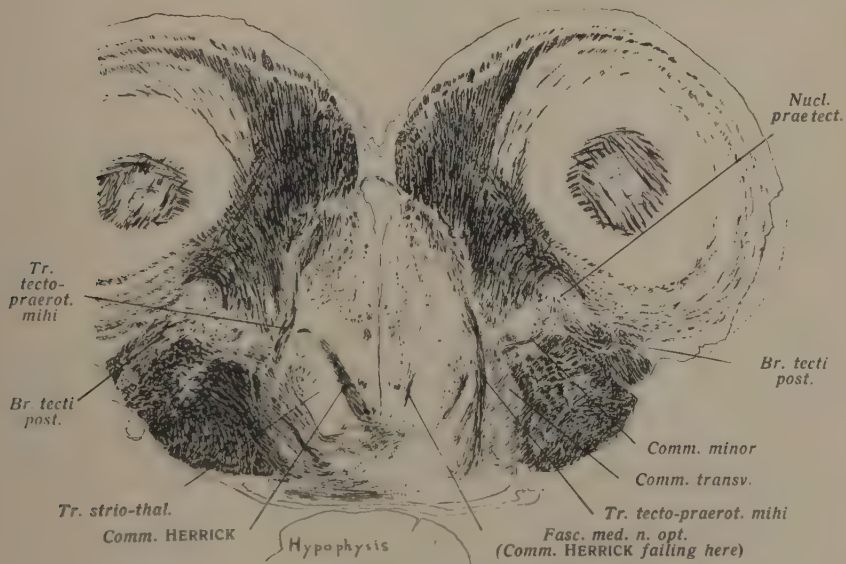


Fig. 2. Mugil chelo.

(Preparation of the Central Institute for Brain-research, Amsterdam).

Gasterosteus (see fig. 3), double-sided in a specimen each of *Belone* and *Exocoetes*). However, I want to consider this course as aberrating, for in another specimen of *Gasterosteus* and also of *Exocoetes* it runs laterally to the tr. strio-thalamicus, as with the other Teleosts.

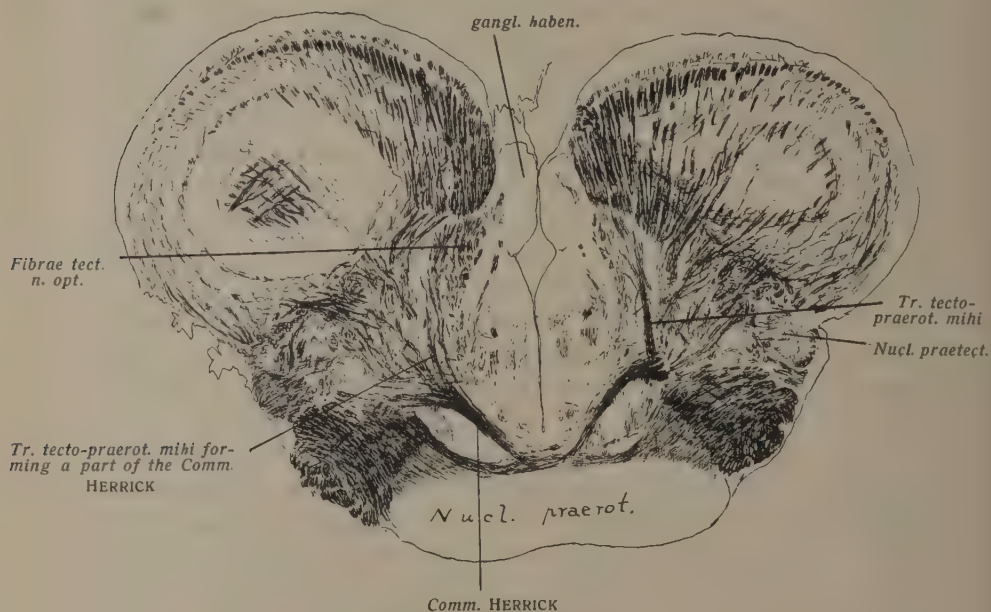


Fig. 3. *Gasterosteus aculeatus*.

(Preparation of the Central Institute for Brain research, Amsterdam).

Ventrally it mixes, as mentioned, among the fibres of the commissura transversa, in two ways. One time it runs nearly horizontally towards medial as the most caudal part of this commissure, close to the ventral periphery of the midbrain. Here it soon cannot be traced any further among the commissure fibres. Yet it seems plausible to me that here it crosses the medial line. This I find with *Trutta*, *Syngnathus*<sup>?)</sup>, *Ammodytes*<sup>?)</sup>, *Mugil*, *Ophiocephalus*, *Morone*, *Osphremenus*, *Pleuronectes platessa*<sup>?)</sup>, *Rhombus*, *Hippoglossus*<sup>?)</sup>, *Solea*<sup>?)</sup>, *Cyclopterus*, *Agonus*<sup>?)</sup>, *Trachinus* and *Tetrodon*.

Another time it forms the most dorsal part of the commissura transversa and crosses directly under the ventricle. I was able to ascertain this course, besides in the cases where it is delusive of the commissura minor (*Gasterosteus*, *Belone* and *Exocoetes*), with

<sup>1)</sup> The question-marks denote that with these Teleosts I do not find the matter quite clear.



*Clupea*?<sup>1)</sup> and *Pleuronectes limanda*. Also with *Gadidae* this tract can easily be traced from the subventricular crossing as far as the deep medullary layer of the tectum.

FRANZ has erroneously indicated this bundle in *Gadus*, in fig. 6 of his work, as "fibrae tect. n. opt." The correctness of my observation, however, can be tested not only in *Gadus* itself, but very easily in *Lota* and *Motella*. In fig. 24 of the same work FRANZ has called the same tract correctly "ascending decuss. transversa" (the upper line of his reference, at the bottom, left hand).

Although the exact way of origin and termination of this bundle is not yet clear to me, I should like to call it provisionally *tr. tecto-praerotundus* and introduce it under this name.

### III. *Tr. isthmo-praetectalis*.

FRANZ describes the course of his *tr. isthmo-opticus* as follows (op. cit., p. 414): "a tract which, together with the opticus, first appears ventrally to the midbrain roof, ascends on the inside of the midbrain roof, reaches the torus semicircularis and here curves round to the ganglion isthmi — here often difficult to distinguish from the fibres of the commissura transversa. It may be possible that part of the fibres remains already in the torus semicircularis."

He further is of opinion, supported by experiments (on which fishes?) that the fibre tract arises undoubtedly from cells of the ganglion isthmi and sends its neurites centrifugally into the eye (i.e., p. 415).

My investigation confirms the presence of such a bundle and its caudal course, as described by FRANZ. I only want to remark that I could not find this bundle with all bony fishes. A few fishes, such as Salmonids, Siluroids, *Misgurnus*, *Symbranchidae*, *Esox*, *Ammodytes*?<sup>1)</sup>, *Gadidae*, *Lophius*?<sup>1)</sup> and *Tetrodontidae*?<sup>1)</sup> seem not to possess such a fibre tract.

Its further frontal course, however, is not as supposed by FRANZ, but different according to the Teleosts examined.

FRANZ seems to be right, in so far as the bundle, after its characteristic curve in the torus semicircularis, gathers its fibres at the lateral basal ridge of the midbrain, then by bundles enters into the lateral opticus root and disappears from examination under the fibres of the latter, as is the case with *Megalops* (with all?<sup>2)</sup>), *Gastero-*

<sup>1)</sup> The question-marks indicate here that the matter concerned is not quite clear in these fishes.

<sup>2)</sup> The brackets refer to the quantity of fibres, entering into the opticus root.

steids (few)<sup>2)</sup>, Scombresocids (part)<sup>2)</sup>, Mugil (the greater part)<sup>2)</sup>, Ophiocephalus (the greater part)<sup>2)</sup>, Morone (greater part)<sup>2)</sup>, Osphromenus (part)<sup>2)</sup>, Cottids?<sup>1)</sup>, Cyclopterus?<sup>1)</sup>, Agonus?<sup>1)</sup> and Trachinus (with the smaller part of the fibres)<sup>2)</sup>.

On the other hand there are bony fishes in which the bundle in question can be distinctly followed as far as the frontal tectum section, as Clupea, Cyprinidae, Syngnathidae, Osphromenus, Pleuronectidae (Solea excepted) and Callionymus. I therefore will give here a minute description of the course of this fibre tract in some specimens of fishes.

Just with *Pleuronectes*, where FRANZ believed to have his tr. isthmo-opticus fully established, we can clearly prove that the bundle in question actually enters frontally into the tectum, in the most superficial medullary fibre layer of it. The small bundles namely gather on the lateral surface of the midbrain to a roundish bundle that protrudes into the optic ventricle and then takes a wholly sagittal course. (see fig. 6 of *Hippoglossoides*). At first it runs ventrally to the bundles of tr. tecto-bulbaris and directly dorsal of the ventral point of the tectum plate. Some way more frontal it takes the shape of a curved medullary plate and encircles about half of the nucl. praetectalis from the lateral side. During this course its position corresponds to the bottom of the tectal furrow characteristic of this fish and, situated caudally deep inside, it frontally more and more approaches the outer surface; at last, quite frontal on the level of the geniculatum, it comes close under the molecular layer<sup>3)</sup> of the tectum. Till there it never touches the opticus root. Now part of the bundle radiates caudo-laterally of the geniculatum, towards medio-dorsal into the dorsal part of the tectum<sup>4)</sup>, whereas the other part runs further frontad and finally enters latero-ventrally into connection with the ventral part<sup>4)</sup> of the tectum, which extends a little further frontad than the dorsal one. At this radiation of the bundle I could quite clearly distinguish its small bundles from those of the brachium tecti (KAPPERS) and the optic root, and prove that the most superficial narrow layer of the so-called opticus fibre layer of the tectum consists of the little bundles of the fibre tract in question and the next much broader layer of medullary fibres (of the opticus

<sup>1)</sup> See note 1 p. 71.

<sup>2)</sup> See note 2 p. 71

<sup>3)</sup> This designation has its explanation in the above-mentioned treatise „On the torus longitudinalis etc.”.

<sup>4)</sup> The frontal part of the tectum plate is divided into two parts by the aforementioned furrow.

fibre layer), separated from the first by a strand of grey substance, consists of the small bundles of the brachium tecti and the tr. opticus (see fig. 4).

Also with Clupea, examined likewise by FRANZ and drawn by him in fig. 9 of his treatise, I could trace the fibre tract as one or two coarsefibred bundles above and partly through the lateral opticus root, lateral of the praetectal nucleus and the geniculatum, as far as in the upper fibre layer of the most frontal tectum (fig. 5).

With the Cyprinidae its course is about the same as with Clupea. The small bundles gather medio-dorsally to the lateral root in one or two bundles, then run frontad, at first between the nucl. praetectalis and the lateral opticus root, then between the nucl. anterior thalami and the ganglion geniculatum. Here a part of the fibres branches off into the tectum, but the remainder runs, dorsally to the geniculatum, further frontad, then turns medio-dorsad and finally also reaches the tectum.

By the way I want to remark that with these Teleosts (Pleuronectids, Clupea and Cyprinids) the bundle in question is accompanied in its entire frontal course by the tr. geniculo-myelencephalicus of HOLMGREN. The two bundles, however, can easily be distinguished, the fibres of the first bundle being far coarser than those of the latter.

With Osphromenus the bundle shows a peculiarity. Part of its fibres enter, as mentioned above, already caudally into the lateral opticus root. Here again I expected to be able to trace the small bundles through the complex of the opticus fibres right into the upper fibre layer of the tectum. The other part, however, turns in the subependymal layer gradually medio-dorsad, above the comm. horizontalis fibre group<sup>1)</sup>, and finally enters into the fibre system of the most medio-frontal tectum part.

Therefore I am fully convinced that there is no doubt but the bundle in question, that is to say what FRANZ calls tr. isthmo-opticus, does not run in the opticus to the eye, as FRANZ presumes, but to the frontal tectum, and there becomes part of the opticus fibre layer. Also in those cases where the fibres concerned enter already caudal into the lateral opticus root, it may be assumed that we have the same state of affairs as I have been able to prove in Osphromenus. In the following I shall call the bundle provisionally *tr. isthmo-tectalis*, although the direction of its course (ascending or descending) is not have proved yet.

<sup>1)</sup> Complex of commissura horizontalis and tr. tecto-cerebellaris (cf. fig. 5).

This *tr. isthmo-tectalis mihi* was traced already fairly minutely by MAYSER, the sharp observer. He called it "the outer (back) layer of the stratum zonale" of the torus semicircularis; but made it originate frontal in the corpus geniculatum externum (nuc. prae-tectalis of the authors) and terminate caudally between "numerous

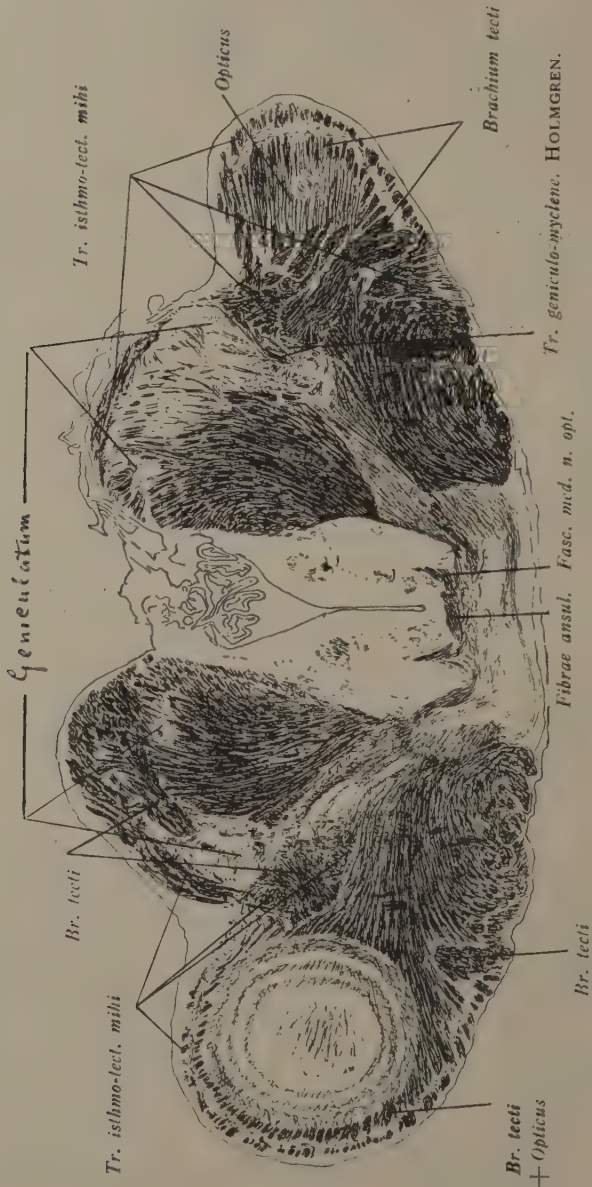


Fig. 4. *Pleuronectes platessa*.  
(Preparation of the Central Institute for Brainresearch Amsterdam.)



small nerve cells chiefly in the caudal and upper part of the torus" (op. cit., p. 342—343 and 348), without yet having applied to the latter a special name (ganglion isthmi).

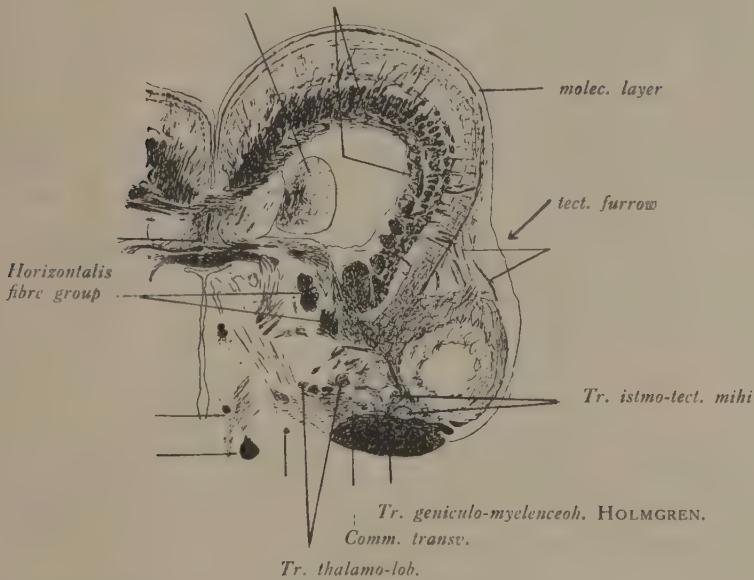


Fig. 5. *Clupea harengus*.

(Preparation of the Central Institute for Brain research, Amsterdam.)

After MAYSER no authors had occupied themselves, as far as I know, with this interesting fibre bundle, till FRANZ discovered it again.

Through the result of this investigation the relation between the tectum opticum and the ganglion isthmi with Teleosts gets closer. The connection is twofold, one time through the tr. tecto-isthmicus of FRANZ, another time through the tr. isthmo-tectalis of myself, and we may presume that the first leads tectofugal, the latter tectopetal.

Although MAYSER's opinion that the bundle in question originates from the corpus geniculatum externum s. l. (i.e. from nucl. praetectalis of the authors) cannot be confirmed by me as to the Cyprinoids (s. above), yet I saw in a specimen of *Exocoetus* a small part of the fibres of my tr. isthmo-tectalis end in the nucl. praetectalis, the other larger part running further frontal past this nucleus. The same I have been able to find with *Cyclopterus*, *Trachinus*, with some doubt also with the Gasterosteids, Syngnathidae, *Belone* and *Solea*. As just on the spot where these fibres should enter and end

in the nucl. praetectalis, the brachium tecti, whose fibres are as coarse as the others, leaves this nucleus, it is quite possible that a misinterpretation can arise. All the same I can maintain this point as being quite certain, at least with *Exocoetus*. When this is the case, these fibres correspond with those of CATOIS from the nucl. praetectalis, of which he writes: "Les autres (fibres)<sup>1)</sup> descendent presque verticalement de la partie inférieure du noyau prétectal, se recourbent ensuite en arrière et se dirigent vers la région basale du mésencéphale" (op. cit., p. 97). But when he supposes "qu'elles doivent servir à établir des connexions entre le thalamus et la moelle spinale" (i.e., p. 97—98), this remains a mere supposition, for according to my investigations we can say for certain that they are connected with in the ganglion isthmi and consequently form a *tr. isthmo-praetectalis*,<sup>2)</sup> (or *praetecto-isthmicus*).

#### IV. *Pars praetectalis Comm. posterioris.*

The component part of the so-called "*stratum zonale*" of the torus semicircularis, (for convenience' sake I here use this long abandoned nomenclature) is not at all exhausted with the above *tr. isthmo-tectalis mihi* and the commissura transversa. With most bony fishes there is namely a fibre connection between this stratum and the commissura posterior. One bundle from about the middle of this commissure runs latero-ventrally and at the same time frontad, joins the *tr. isthmo-tectalis* in the most caudal level of the nucl. praetectalis (fig. 6) or, if this is missing, directly the commissura transversa and then joins in the characteristic curved course of the torus semicircularis. To the first category, where there is a *tr. isthmo-tectalis*, belong the Gasterosteids, *Belone*, *Mugil*, *Ophiocephalus*, *Morone*, *Osphromenus*, *Pleuronectids*, *Gobius*, *Cottus*, *Cyclopterus*, *Agonus*, *Trachinus* and *Callionymus*, to the latter, where the *tr. isthmo-tectalis* is not present, belong *Symbranchidae*?, *Esox*, *Ammodytes*, *Gadids*, *Solea*, *Lophius* and *Tetrodontidae*. The fibres of the latter bundle are thinner than those of the *tr. isthmo-tectalis*. On the other hand there are fishes that have no such connection, e.g. *Megalops*?, *Clupea*, *Cyprinoids*, *Syngnathidae*, *Exocoetus* and *Zoarces*?

This bundle differs from the other components of the commissura posterior by its finer fibres and mostly also by its compactness. As to its position it is about in the middle of the commissure, in sagittal

<sup>1)</sup> Bracketed by myself.

<sup>2)</sup> Cf. also HOLMGREN'S drawings of *Callionymus*: fig. 87, 88 and 89: *Tr. ist.-praet.*

as well as in dorso-ventral direction. In WEIGERT-preparations it often has a greyish colour, which makes me suppose that it consists of medullary as well as unmedullated fibres.

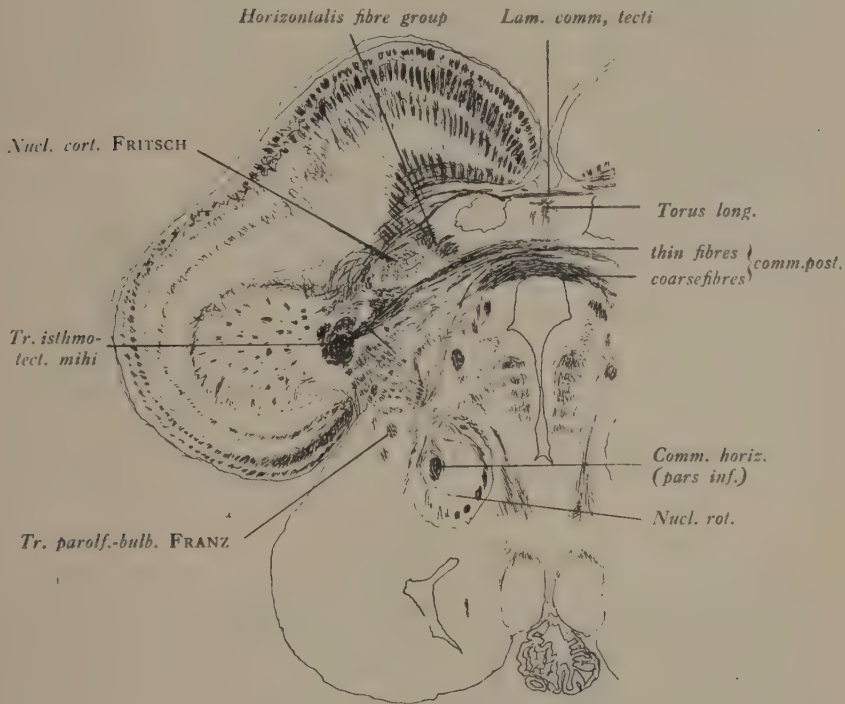


Fig. 6. *Hippoglossoides platessoides*.  
(Preparation of Prof. RÖTHIG's Collection, Berlin.)

ARIËNS KAPPERS in his work on Ganoids (op. cit., p. 475) has expressed the supposition that the middle part of the commissura posterior partly enters into a connection with the geniculatum (i.e. the nucl. praet-ectalis of the authors), partly passes over this nucleus, bends backwards and ends in the tegmental region, just under the torus semicircularis. Also in his treatise on the brain of *Chimaera* (p. 158) and of late in his manual (p. 818) he considers it as highly probable that this "lateral part" of the commissura posterior originates in the geniculatum (i.e. in the nucl. praetectalis) of the one side and extends caudad on the other side (extremely clear with *Pleuronectidae*, as he emphasizes).

HOLMGREN calls the relative part of the commissura posterior after EDINGER commissura praetectalis, but is also of opinion that it is "not excluded that praetectalis fibres, that were traced till in the

commissura posterior, may go on the other side to an other final station than in the nucleus praetectalis" (op. cit., p. 262).

In my opinion one of the two formations is to be considered as the caudal destination of this bundle, viz. the torus semicircularis or the ganglion isthmi, the first with greater probability than the latter. About its frontal extremity I cannot express an opinion for the present, although the nucl. praetectalis of the other side seems to be the most probable. In any case further investigations on this point are most desirable.

It is difficult yet to say anything about the relation of the bundle concerned, to the commissura praetectalis (or pars praetectalis of the commissura posterior) of EDINGER. However, I have been able to state with a specimen of *Leuciscus rutilus* that, although with no other of the Cyprinoids which I examined, I could prove a well-marked fibre connection between the commissura posterior and the tr. isthmo-tectalis mihi or even the "stratum zonale" of the torus semicircularis, with the said fish there existed a well characterized, closed commissura bundle between the nuclei praetectales of both sides.

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**Chemistry.** — "*n.α-Sulphobutyric acid and its optically active components*". By Prof. H. J. BACKER and J. H. DE BOER. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of January 27, 1923).

After it had been shown that α-sulphopropionic acid can be separated into its optically active components<sup>1)</sup>, we tried to effect this resolution also for norm. α-sulphobutyric acid. At the same time the occasion was taken to study this acid, which has been known already since 1875, but hitherto had not been obtained in a pure crystallised state.

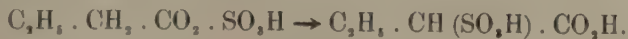
The acid is formed by direct sulphonation of n.α-butyric acid or of butyric anhydride<sup>2)</sup>.

Just as in the case of the propionic acid, the sulphonic acid group is attached to the α-carbon atom, as proved by its relation to α-bromobutyric acid, of which the structure is fixed.

HEMILIAN caused the ester of this acid to react with ammonium-sulphite and we have applied this reaction to the free α-bromobutyric acid; in both cases the same sulphobutyric acid was formed as by direct sulphonation.

We also obtained the sulphobutyric acid in a good yield (70 %) from ethylmalonic acid, which by sulphonation loses one molecule of carbon dioxide. Besides, this formation may serve as an argument for the structure, the active hydrogen atom of the ethylmalonic acid having the greatest chance of being substituted by the sulphonic acid group.

As a method of preparation we used the sulphonation of the carefully fractionated n. butyric acid with sulphur trioxide. In the cold butyrylsulphuric acid is formed, which on heating passes into sulphobutyric acid:



The acid was separated in the form of its barium salt, which was purified by crystallisation, and from which sulphuric acid liberated again the organic acid.

<sup>1)</sup> FRANCHIMONT and BACKER, These Proceedings **17**, 653 (1914); Recueil d. trav. chim. **39**, 751 (1920).

<sup>2)</sup> HEMILIAN, Ann. d. Chemie **176**, 2 (1875). FRANCHIMONT, Recueil d. trav. chim. **7**, 27 (1888). VAN PESKI, Recueil **40**, 736 (1921).

Sulphobutyric acid was hitherto only known as a viscous liquid. We succeeded in obtaining the acid in the crystallised state by leaving a concentrated pure solution for a long time in vacuo over phosphorus pentoxide.

The  $\alpha$ -sulphobutyric acid forms colourless hard crystals. Like sulphoacetic and sulphopropionic acids it contains one molecule of water of crystallisation and is extremely hygroscopic. The melting point, determined by the aid of a formerly described apparatus<sup>1)</sup>, was found to be 66°.

Since sulphoacetic acid melts at 84—85° and sulphopropionic acid at 100.5°, we have here perhaps the beginning of an alternating series of melting points, as shown by the fatty acids.

From sulphobutyric acid we have prepared some salts with aromatic amines.

The acid sulphobutyrate of aniline forms small glistening crystalline plates with the melting point 175°.

The acid sulphobutyrate of *p*-toluidine, which is separated by ether from its alcoholic solution in the form of an ethergel, may be obtained as a white crystallised substance of the melting point 163°.

The acid salts of *p*-anisidine and *p*-phenetidine were obtained in a crystallised state, but not pure and colourless.

If these sulphobutyrate are heated with an excess of the corresponding amines, the carboxyl group is changed into amide through loss of water, the sulphonic acid group remaining combined with a molecule of the amine.

In this way aniline formed the *butyranilide- $\alpha$ -sulphonic acid salt of aniline*



which crystallises from water in concentrically grouped featherlike needles, occasionally 5 cm. in length, which melt at about 253°—256°.

From the other above mentioned aromatic amines well crystallised amides were also obtained, viz.

*butyro-p-toluidide- $\alpha$ -sulphonic acid salt of p-toluidine*, m.p. 260—263°,

*butyro-p-anisidide- $\alpha$ -sulphonic acid salt of p-anisidine* m.p. 242°,

*butyro-p-phenetidide- $\alpha$ -sulphonic acid salt of p-phenetidine*, m.p. 264—266°.

When heated with aromatic o-diamines, sulphobutyric acid, just as sulphopropionic acid, loses two molecules of water and gives derivatives of benzimidazole.

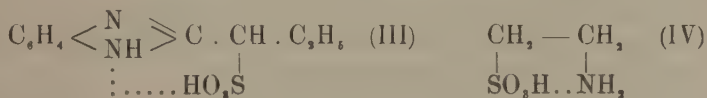
The sulphobutyrate of o-phenylenediamine, for instance, formed

<sup>1)</sup> Chem. Weekbl. 16, 1564 (1919).

on heating at  $180^{\circ}$  *benzimidazole-2-propylsulphonic acid* (I), whilst from the sulphobutyrate of 3,4-diaminotoluene was formed in the same way *methylbenzimidazole-2-propylsulphonic acid* (II).



These imidazoles were obtained as white crystalline substances. They are almost insoluble in the common solvents, have a very high melting point, and, notwithstanding the presence of a sulphonic acid group, they do not combine with aromatic amines and they are not hygroscopic. All these properties indicate, that the sulphonic acid group forms an internal salt with the basic function of the imidazole (III) and they completely recall the properties of taurine, for which an analogous structure is assumed (IV).



With strong bases, such as baryta, these imidazolesulphonic acids give well crystallised salts. From the barium salt and copper sulphate a green solution is formed, which, however, decomposes immediately when heated and also when kept for a long time at the ordinary temperature, so that the copper salt could not be separated in a crystallised pure state. It deserves attention, that, in spite of many efforts, also no copper salt of taurine has been obtained.

The resolution of racemic  $\alpha$ -sulphobutyric acid was attempted with the aid of strychnine, by reason of previous experience with sulphopropionic acid, and the attempt was successful.

The acid strychnine salt of the d-acid is less soluble than the salt of the l-acid, just as in the case of sulphopropionic acid.

After three or four crystallisations the acid strychnine salt of the d-sulphobutyric acid is entirely free from the other component. It crystallises with two molecules of water in small glistening needles.

On concentration, the first mother liquor slowly gives a crop of the acid strychnine salt of l-sulphobutyric acid, which by repeated crystallisation from alcohol is obtained in a pure state.

Decomposition of the strychnine salts by baryta gives the barium salts of the active acids.

These barium salts crystallise from water in long needles which contain  $2\frac{1}{2}$  molecules of water, in contradistinction to the racemic barium salt, which separates in small glistening leaflets with two molecules of water of crystallisation.

The direction of the rotation of the neutral barium salts is, as in the case of sulphopropionic acid, opposite to that of the free acids.

The molecular rotatory power depends on the concentration; on dilution it rises a little. The barium salts, for instance, give in a  $2\frac{1}{2}\%$  solution for sodium light a molecular rotation of  $32.2^\circ$  and in a  $5\%$  solution a rotation of  $29.9^\circ$ . In a  $2\frac{1}{2}\%$  solution the presence of  $10\%$  of barium chloride lowers the molecular rotation to  $29.3^\circ$ .

This indicates, that the rise of the molecular rotation on dilution may be ascribed to an increasing of the ionisation, a phenomenon, which is perhaps connected with the fact that the sign of rotation of the neutral salts is opposite to that of the free acids.

The molecular rotation of the free salts for sodium light is  $7.8^\circ$ .

The acid salts rotate the plane of polarisation in the same direction and to about the same amount as the free acids.

In this respect also, the behaviour of sulphobutyric acid is therefore analogous to that of sulphopropionic acid.

The investigation is being continued and will be published later in greater detail.

Groningen. 13 Jan. 1923.

*Organic Chemical Laboratory of  
the University.*

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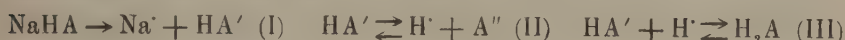
**Chemistry.** — ‘*The second dissociation constant of sulphoacetic and  $\alpha$ -sulphopropionic acids.*’ By Prof. H. J. BACKER. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of January 27, 1923).

The determination of the second dissociation constant of a dibasic acid  $H_2A$  from the concentration of the hydrogen ions in the solution of an acid salt readily suggests itself.

However, A. A. NOYES <sup>1)</sup> has shown, that generally these data will not suffice.

Suppose that the ionisation of the acid sodium salt (reaction I) is nearly complete, and that the concentration of the  $HA'$  ions, which according to reaction II are partly split further, may be identified with the concentration of the acid salt dissolved, we must nevertheless remember that the number of hydrogen ions will decrease by combination with the ions  $HA'$  (reaction III).



This last reaction will be especially noticeable, when the acid is weak, which is indeed the case with all organic acids examined in this respect.

The sulphocarboxylic acids, however, are examples of strong dibasic acids, which at small dilutions are already well ionised. Therefore, we may expect, that the consumption of hydrogen ions for formation of the free acid will only have a small influence, so that from the concentration of the hydrogen ions the degree of dissociation of reaction II may be determined, and further the dissociation constants.

NOYES has given the following general formula for the acid salts of dibasic acids:

$$k_2 = \frac{(k_1 + c + H) H^2}{k_1 (c - H)}$$

$k_1$  and  $k_2$  are the first and second dissociation constants of the acid,  $c$  is the original concentration of the acid salt (in gram molecules per litre) and  $H$  is the concentration of hydrogen ions (in gram ions per litre).

<sup>1)</sup> Z. f. physik. Chemie 11, 495 (1893).

If  $k_1$  is large compared with  $c$  and  $H$ , we may write:

$$k_2 = \frac{H^2}{c-H}.$$

Now, this expression is identical with OSTWALD'S dilution law,  $k = \alpha^2/(1-\alpha)v$ , as shown by substitution of  $\alpha = H/c$  and  $v = 1/c$ .

This simplification will be permissible in the case of sulphaacetic and sulphopropionic acids, for which, in a previous paper<sup>1)</sup> the first dissociation constants were found to be 0.58 and 0.57 respectively.

Now, the solutions of the acid salts of these compounds in various concentrations were compared, by the aid of indicators, at room temperature, with the buffer solutions of SÖRENSEN and of CLARK.

In the following table  $v$  is the number of litres, containing 1 gram molecule of the acid salt,  $p$  is the hydrogen exponent ( $p = -\log H$ )  $H$  is the concentration of the hydrogen ions in gram ions per litre,  $\alpha$  is the degree of dissociation of reaction II ( $\alpha = Hv$ ) and the equilibrium constant derived therefrom is  $k_2 = \alpha^2/(1-\alpha)v$ .

	$v$	$p$	$H$	$\alpha$	$k_2$
Sulphaacetic acid	16	2.65	0.00224	0.0358	$8.3 \times 10^{-5}$
	32	2.8	0.00158	0.0506	8.4
	64	2.95	0.00112	0.0717	8.5
	128	3.05	0.00089	0.114	11.5
	256	3.25	0.00056	0.143	9.4
	512	3.4	0.00040	0.205	10.3
Sulphopropionic acid	16	2.7	0.00200	0.0320	$6.6 \times 10^{-5}$
	32	2.85	0.00141	0.0451	6.7
	64	3.0	0.00100	0.0640	6.8
	128	3.2	0.00063	0.0806	5.5
	256	3.4	0.00040	0.102	4.5
	512	3.55	0.00028	0.144	4.7

The concordance of the constants at various dilutions is very satisfactory, as the indicator method does not allow a great accuracy.

However, for great concentrations a correction might be made

<sup>1)</sup> These Proceedings 25, 359 (1922).

according to NOYES' formula. For this the values of  $k_2$  must be multiplied by  $(k_1 + c + H) / k_1$ .

This correction only affects the dilutions 16, 32 and 64.

Thus, the following values are found:

	$v = 16$	32	64	128	256	512	mean value.
sulphoacetic acid $k_2 =$	9.1	8.9	8.8	11.5	9.4	10.3	9.7
sulphopropionic acid $k_2 =$	7.2	7.1	7.0	5.5	4.5	4.7	6.0

Little differences in the colorimetric determinations of  $p$  have in this method a great influence on the value of  $k_2$ .

In a simpler way the second dissociation constant of a dibasic acid may be measured by examining a mixture of a neutral and an acid salt<sup>1)</sup>.

If  $\alpha''$  is the degree of dissociation of the neutral salt  $\text{Na}_2\text{A}$  and  $\alpha'$  the degree of dissociation of the acid salt  $\text{NaHA}$ , then the second dissociation constant of the acid may be represented by:

$$k_2 = \frac{\alpha'' \times [\text{Na}_2\text{A}]}{[\alpha' \times \text{NaHA}]}$$

Since these degrees of dissociation for salts are not much smaller than 1, the factor  $\alpha''/\alpha'$  may be neglected in a first approximation.

For the sake of simplicity a solution was taken containing an equal number of molecules of the acid and of the neutral salt, so that  $k = H$ , and this solution was examined at various dilutions.

The concentration of hydrogen ions was again determined by means of the indicator method.

In next table  $v$  is the number of litres containing one molecule of the neutral salt together with one molecule of the acid salt.

The variations of the constant due to dilution are not considerable, but it is remarkable that they are all in the same direction. By dilution the degree of acidity of the solution decreases.

This behaviour indeed agrees with the theory, since for the sodium salt of a dibasic acid the dissociation on diluting increases more than for the sodium salt of a monobasic acid. Therefore the value of  $\alpha''/\alpha'$ , which for infinite dilution must amount to 1, is smaller for the greater concentrations.

The value of  $\alpha''$  follows from the conductivity of the neutral sodium salt at various dilutions, published in the previous paper, and for  $\alpha'$  the above mentioned values may be taken.

<sup>1)</sup> In this way I. M. KOLTHOFF has measured the second dissociation constants of a number of dicarboxylic acids. (Der Gebrauch von Farbenindikatoren, p. 102).

	$v$	$p$	$H = k_2$
Sulphoacetic acid	32	4.0	$10.0 \times 10^{-5}$
	64	4.05	8.9
	128	4.1	7.9
	256	4.15	7.1
	512	4.25	5.6
Sulphopropionic acid	32	4.25	$5.6 \times 10^{-5}$
	64	4.3	5.0
	128	4.35	4.5
	256	4.4	4.0
	512	4.4	4.0

When this correction is made, the following constants are found:

	$v = 32$	64	128	256	512	mean value :
sulphoacetic acid	$k_2 = 8.7$	7.9	7.3	6.7	5.4	7.2
sulphopropionic acid	$k_2 = 4.8$	4.4	4.1	3.7	3.8	4.2

In the preceding paper the second dissociation constants of both acids are calculated from measurements of the conductivity of the acid salts.

In the present paper these constants have been obtained colorimetrically first from the  $p_H$  of the acid salt and then from the  $p_H$  of mixtures of neutral and acid salts.

The mean results of the various methods are collected in the following table.

Methods	Sulphoacetic acid	Sulphopropionic acid
I. Conductivity of acid salts.	$k_2 = 7.4 \times 10^{-5}$	$k_2 = 4.8 \times 10^{-5}$
II. Hydrogen ion concentration of mixtures of acid and neutral salts.	7.2	4.2
III. Hydrogen ion concentration of acid salts.	9.7	6.0



In judging these figures it should be remembered, that each of the methods used here only gives approximative values, which is also evident from the deviations in each series of measurements.

However, the order of magnitude is the same for the constants determined in various ways.

Thus from this research we may conclude, that the second dissociation constant of sulphoacetic acid amounts to about  $1 \times 10^{-4}$  and that the constant of sulphopropionic acid is about one third smaller.

*Groningen, January 1923.*

*Organic chemical laboratory  
of the University.*

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**Zoology.** -- "*Experimental Budding in Fungia fungites*". By Dr. H. BOSCHMA. (Communicated by Prof. C. PH. SLUITER).

(Communicated at the meeting of January 27, 1923).<sup>o</sup>

A large number of the Fungiae to be found on coralreefs display anomalies mostly arising from the destruction of part of the living tissue. In many cases the destroyed stretches of living tissue are attacked by small algae, which penetrate to a considerable depth, and gradually spread into the living tissue. Such decaying spots often stimulate the adjacent tissue, which consequently exhibits a more energetic growth-activity than usual. The result then is that something like a raised rim arises on the border between the living and the defunct part. In many cases this greater activity is also manifested even in the formation of buds. In a previous publication I discussed this budding in adult Fungiae<sup>1)</sup>. Here I also pointed to the fact that algae-parasitism is one of the chief causes of budding in adult corals. Generally the destruction of only a small part of the living tissue suffices for the vicinity to be stimulated to a more energetic growth-activity.

This induced me to endeavour to develop buds experimentally in *Fungia fungites*. My material for this experiment consisted of specimens of *Fungia fungites* from the reef of the island of Edam near Batavia. The most normal corals devoid of buds or other anomalies were selected. To destroy part of the tissue a small piece of putty was pressed into the central region of the oral surface of some fifty specimens on the 18<sup>th</sup> and the 19<sup>th</sup> of August 1921. The putty was held fast on either side of the mouth by the septa. The corals were then restored to their original places.

In this experiment, I expected the destruction of part of the central tissue to extend to the mouth in most of the specimens, as this would most likely bring about a strong reaction to the lesion, so that budding would soon ensue. True, the ingest of food would hereby be slightly impeded. But considering that *Fungia* feeds only partly on organisms other than zooxanthellae, and considering moreover

<sup>1)</sup> H. BOSCHMA, "On Budding and Coalescence of Buds in *Fungia fungites* and *Fungia actiniformis*." Proceedings Kon. Ak. van Wetensch. Amsterdam. Vol. XXIV, 1922.

that the basal portions of the axial groove were not entirely covered, the impediment was not of a serious nature. This experimenting method was most suitable for achieving results in a short time.

After the lapse of nearly four months the putty could still be seen unaltered as to shape, as a hardened substance above the mouth. Some corals had already developed buds. On the 11<sup>th</sup> of December 1921 five specimens were brought back, one of which (N<sup>o</sup>. 464) was preserved in formalin and the other four were left dry (N<sup>o</sup>. 460—463). The changes resulting from the experiment are summarized as follows:

N<sup>o</sup>. 462. About one fifth of the upper surface is defunct. Beneath it buds have developed on the under surface, smaller ones at the margin, larger ones more towards the centre.

N<sup>o</sup>. 463. Half of the upper surface is defunct. Only few septa in this destroyed part exhibit in the margin residues of living tissue. Portions of the margin of the under surface, under the defunct part of the upper surface, are also defunct. The rest is still covered with living tissue. On the upper surface some large buds and many small buds at the margin. (Fig. 1—3).

N<sup>o</sup>. 464. Two opposite quarters of the upper surface devoid of living tissue. The destruction of the soft parts has extended round the margin of the coral, so that here also some portions are defunct. On the under surface a few large buds, a few smaller ones in the margin.

N<sup>o</sup>. 460. On the upper surface the living tissue was quite lost, on the under surface only in some places at the margin. Here a few small buds are to be recognised, while in the more central part a few larger ones have developed.

N<sup>o</sup>. 461. Upper surface quite defunct, under surface still covered with living tissue. In the margin of the under surface many small buds, in the centre a few larger ones.

In all specimens a stretch of the tissue nearest to the putty first died away. This process progressed along the septa to the periphery so that the defunct part assumed the form of a sector of a circle. The decay of the living tissue now spread along the margin on the lower surface, the consequence of which was that the enviroing tissue was stimulated to greater activity and accordingly developed buds.

At the living corals the larger buds, which were located at some distance from the margin, were most conspicuous. (Fig. 3). The diameter of the basal part of these buds varied from 2 to 12 mm. The mouth was invariably small and the height inconsiderable. The spines of the costae of the parent coral were often visible through the thin living portions of the bud. In these large buds the skeleton is still very incomplete. The theca and the first septa are only little developed; on the other hand the columella is already distinguishable in the form of a large number of irregular trabeculae.

In the smaller buds, which were generated principally in the marginal regions of the under surface the development of the skeleton can easily be traced, as the buds differ very much in age. They are of a much more regular structure than the larger ones.

In the youngest buds, with a diameter of about 0.5 mm., nothing of the skeleton is visible except the theca, which appears as a thin wall, stretching obliquely upward and consequently looks like a truncated cone. (Textfig. a).

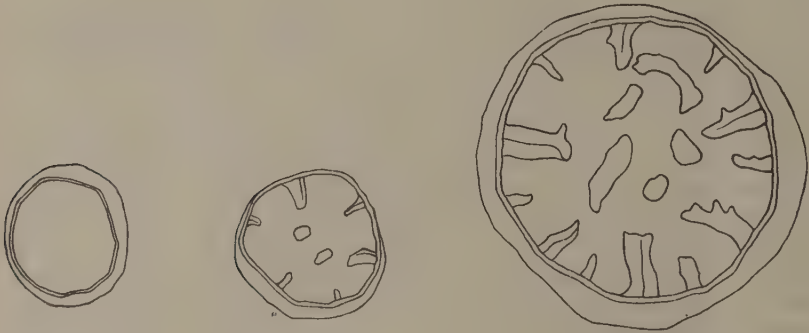


Fig. a.  $\times 45$ .

Fig. b.  $\times 45$ .

Fig. c.  $\times 45$ .

The theca has no perforations, which come forth only in much older buds. Soon after this the first cycle of six septa spring up. They proceed from the theca further towards the centre of the bud. (Textfig. b). The upper rim of the theca rises above the septa. The columella also develops in this phase as short projections in the basal parts of the bud. In buds of this size there are never more than six septa. They originate almost simultaneously, buds with a smaller number of septa occurring only very seldom. The number of similar buds with less than six septa is too small to ascertain whether the septa arise in a definite order.

The next cycle of septa can only be observed in buds of about 1 mm. in diameter. In them the septa of the first cycle have already considerably increased in size and in thickness, and are already provided with some dentations. (Textfig. c). Likewise the columella has grown larger in this stage. The septa of the second cycle are distinguishable at first sight from those of the first cycle by their being less developed and being shorter. The bud has now attained the length of the youngest stage described by BOURNE<sup>1)</sup>,

<sup>1)</sup> G. C. BOURNE, On the Postembryonic Development of Fungia. Transact. Roy. Dublin Soc. Vol. V, 1893.



to which it bears great resemblance. The further development of these buds resembles that of the buds of an anthocormus.

With the exception of the five specimens that were brought back in December 1921, the other *Fungiae* remained on the reef during nearly nine months. On the 2<sup>nd</sup> of September, when the experiment had been going on for more than a twelvemonth, the specimens that could still be found, were collected. The putty was still in the central part of the oral surface; in the majority of cases the form was unaltered.

In most corals at least some part of the oral surface had lost its living tissue, in a few cases only the plug of putty had caused little or hardly any change. The aspect of the *Fungiae* was now as follows:

Nos. 507, 510, 519 and 520. The aspect of the corals was very normal, without defunct parts. No budding.

Nº. 518. Living tissue normal. The central parts of some septa have risen and have longer dentations. This is owing to the occurrence of new mouths by the side of the old mouth, as was easy to see in the two following specimens.

Nº. 509. No parts of the living tissue destroyed. The central extremities of many septa have grown higher in those places which were in contact with the putty and new mouths have been developed beside these elevations of the septa. The new mouths are now entirely surrounded by septa; on the one side by long regular ones (the original septa of the parent-coral) on the other side by higher parts of recent origin. These parts are somewhat irregular in shape; also the dentations are longer than those of the original septa.

Nº. 508. Covered all over with living tissue. On either side of the old mouth-fissure a few young buds had developed, whose mouths lay between the normal longer parts of the septa and the higher irregular parts that originated later on. (Fig. 5). This specimen is very much like Nº. 509, in which the young septa between the new mouths and the putty are also provided with long dentations.

Nº. 521. Few alterations. The living tissue has disappeared only from the central parts of some contiguous septa. Budding is absent.

Nº. 512. Some adjacent septa devoid of living tissue, further no alterations. No budding.

Nº. 506. Upper surface with two defunct parts, the larger of which covers nearly one fifth of the surface; the smaller part is a narrow streak from the mouth to the margin of the coral. The larger part of destroyed tissue overlaps the margin and covers a small portion of the under surface. At the margin two stemmed young buds have taken origin. The diameter of the disc is respectively 2,5 en 3 m.m. In the defunct part on the under surface there are a few smaller buds.

Nº 501. Almost half of the upper surface defunct, just as a smaller part of the under surface, especially the margin under the destroyed portion of the upper surface. On the boundary between the living and the destroyed part of the under surface, five buds have developed still completely encircled by living tissue of the mother-coral. They are very regular and distinctly stemmed. The diameter of the disc, which in all of them is already broader than the stem, amounts to 6, 7.5,

10.5, 8.5 and 6 m.m. In the defunct marginal part of the under surface there are some smaller younger buds (diameter 1 to 3 m.m.), which, however, have lost their living parts.

Nº. 500. Along the shorter diameter of the corallum a broad band of the upper surface has lost its living tissue. In the living part some septa exhibit a more energetic growth of the central part; however, new mouths could not be distinguished as yet. The parts of the margin of the under surface contiguous to the defunct part of the upper surface had lost their soft portions. In their vicinity buds had developed in the living tissue, five on one side and two on the other (Fig. 4). These buds are less regular in form than those of Nº. 501. Their stages of development differ. The dimensions are:  $13 \times 8$ ,  $7.5 \times 7$ ,  $4.5 \times 4$ ,  $6 \times 5.5$ ,  $5 \times 4$ ,  $13.5 \times 8.5$ , and  $10 \times 7$  m.m. They are fixed to the parent coral by a broad base. The septa of the youngest buds, which are still little developed, are distinguishable from the spines of the costae of the mother-coral by their flattened shape. In the basal parts of most of these buds the spines of the mother-coral are still unaltered. In the destroyed part of the margin, with the five buds, a stemmed bud has developed (diameter of the disc 4.5 m.m., of the stem 3.5 m.m., height 3.5 m.m.). Besides these there are still remains of a number of smaller ones, whose living tissue has, however, disappeared.

Nº. 511. Only one third of the coral was covered by living tissue on the upper surface as well as on the lower surface. In the defunct portion of the lower surface a great many buds had arisen, most of which were still alive. The diameter of these buds ranges from 1 to 3 m.m.

Nº. 502. Of the upper surface only a small part of the margin was still covered with living tissue; of the under surface almost one fourth was still alive. In this part there are in the vicinity of the defunct region four large buds, only two of which possess well-developed septa. The dimensions are  $10 \times 7$ ,  $7 \times 6.5$ ,  $9.5 \times 7.5$ , and  $10 \times 9$  m.m. The buds are not yet stemmed, so that the basal parts of the septa are still fixed over their whole length to the skeleton of the mother-coral. The septa of the youngest buds are distinguishable from the spines of the costae of the mother-coral only by their flattened shape. Besides these large buds there are at the margin, now surrounded by the destroyed region, two stemmed buds with a disc, 3 and 2.5 m.m. in breadth. Moreover a few smaller ones are also visible in the marginal part.

Nº. 514. Upper surface without living parts. However, the tissues of a fourth part had died off quite recently, the skeleton of this part still being little overgrown with algae and other organisms, in contradistinction to the remaining part. At the margin of the part that died off long ago some few young, stemmed buds have developed, which however, have likewise lost their living tissue. The under surface still possessed rests of living tissue beneath that portion of the upper surface, which kept alive longest. Then follows a broad edge from which nearly all soft parts had disappeared. Here some large buds have developed (diameter up to 6.5 m.m.). Little is to be seen as yet of the skeleton. In the remaining part of the under surface, which had been defunct longer, the remains of many small buds are visible, none of which were alive any more.

Nº. 516. Upper surface devoid of living tissues in the margin a few short-stemmed young buds. Under surface still covered with living tissue. In the margin a few young buds of small dimensions, still completely encircled by living tissue of the parent-coral.

Nº. 513. Living tissues entirely disappeared from the upper surface; on the under

surface about one third defunct. In the marginal stretches, where the soft parts have disappeared, a few young buds, most of which are stemmed. Diameter of the disc of these buds up to 3 m.m. In the part of the under surface, which is still covered with living tissue, there occur a large number of buds in all stages of development. The size ranges between 0.5 and 3.5 m.m. The stages represented in the textfigures are also perceptible in many buds.

Nº. 505. The upper surface as well as the under surface without living tissue. At the margin some buds occur; the disc of the largest bud has a diameter of 7 m.m. On the under surface of the coral many young buds in different stages of development.

Nº. 517. This specimen happened to lie upside down. It had lost its living tissue on both sides. On the aboral surface (now the upper surface) no buds had formed, on the oral surface there are eight buds, some of which are already stemmed. The diameter of the disc of these buds varies from 2.5 to 5.5 m.m.

It appears from the foregoing that the results are very different. In some cases the destruction of part of the living tissues had an influence only on the immediate vicinity, where the tissue was consequently brought to greater activity. This appeared from the formation of new mouths beside the old one which had got lost, and of small septa between the new mouths and the defunct part.

Owing to the experiment a smaller or a greater part of the remaining living tissue of the *Fungia* had been destroyed. This process began invariably at central parts of one or more septa, i.e. beside the putty. When the central part of a septum has lost its living tissue, this process progresses towards the periphery and farther along the margin to the under surface of the coral. Of the decaying tissue some isolated parts keep alive and buds issue from them. At the margin of the mother coral these buds are small and of a regular shape; they develop like buds of an anthocormus.

Regarding the development of the skeleton a few remarks may follow here. According to BOURNE<sup>1)</sup> the twelve first septa of *Fungia* originate simultaneously, as is also the case with *Astroides*. In the former, however, the six septa of the first cycle come first and then those of the second. Since the development of the buds is so very regular and the older stages are quite similar to those of the buds of an anthocormus, it may be expected that the first stage of development of the skeleton of the young *Fungia*e, which arise from planulae, is similar to that of the youngest buds here described.

Moreover the youngest stages of *Fungia patella* described by GARDINER<sup>2)</sup> possess no more than six septa, while the older stages

<sup>1)</sup> loc. cit.

<sup>2)</sup> J. STANLEY GARDINER, On the Postembryonic Development of *Cycloseris*. Willey's Zoological Results. Pt. II, 1899.

bear a striking likeness to the young *Fungiae*, described by BOURNE. VAUGHAN<sup>1)</sup> also points out that it has not yet been proved that the first twelve septa of *Fungia* appear simultaneously.

In the development of *Caryophyllia*<sup>2)</sup> there is one stage in which the skeleton agrees very much with the stage illustrated in Textfig. *b*. However, the preceding processes differ in the two corals; whereas in *Caryophyllia* the septa are formed prior to the theca, the reverse takes place in *Fungia*. In *Caryophyllia*, therefore, the septa have outgrown the theca much sooner than in *Fungia*.

So while a great number of small buds appear at the margin, and several large ones on the under surface, the tissue is dying off by slow degrees. The result is a defunct specimen with a large number of living buds of different age. Many authors<sup>3)</sup> look upon such buds on defunct specimens of the same species as having originated from larvae.

In a previous paper I advocated my view that these young *Fungiae* must be considered as buds<sup>4)</sup>. My experiment yielded all sorts of intermediate stages between normal specimens and defunct ones with buds. The large buds that may arise on the aboral surface, are in their earliest phase so large already (up to 12 mm. in diameter) that it is a priori highly improbable that they should have been formed from larvae. Besides the lateral tissues of the bud are connected with those of the parent, while the basal living parts of the bud overlie the skeleton of the old coral, which results from the way in which the columella is formed in these buds. The trabeculae of their columella namely are generated between and on the unaltered spines of the costae of the parent coral.

In the above description the young individuals, which resulted

<sup>1)</sup> T. WAYLAND VAUGHAN, Recent Madreporaria of the Hawaiian Islands and Laysan. Smithsonian Institution, U. S. Nat. Museum, Bull. 59. 1907.

<sup>2)</sup> G. VON KOCH, Entwicklung von *Caryophyllia cyathus*. Mitt. Zool. Stat. Neapel, Bd. XII, 1897. (The stage alluded to is reproduced in Fig. 14).

<sup>3)</sup> S. STUTCHBURY, An Account of the Mode of Growth of Young Corals of the Genus *Fungia*. Trans. Linn. Soc. London, Vol. XVI, 1833.

H. N. MOSELEY, Notes by a Naturalist on the Challenger. London, 1872.

L. DÖDERLEIN, Die Korallengattung *Fungia*. Abh. der Senckenb. naturf. Ges. Bd. XXVII, 1902.

Also the youngest stages of *Fungia patella*, described by GARDINER (loc. cit.) are probably buds of a specimen, of which the remaining part of the living tissue had been destroyed.

<sup>4)</sup> loc. cit. SAVILLE KENT (The Great Barrier Reef of Australia. London, 1893) also deems it most probable that these young *Fungia* are buds, originating from the remains of the living tissue.



from the destruction of stretches of living tissue, have been called buds. Theoretically however, none of these individuals can be considered as buds. In budding the parent remains intact, the buds are generated through a local intensified growth at the body of the parent (DEGENER<sup>1)</sup>). The animal, on which the young individuals grow, is now only a remnant of what it was before. The process of development of the young individuals under consideration, is rather to be defined as a fragmentation, as it has been termed by KORSCHULT and HEIDER<sup>2)</sup>. Small portions of the tissue of the body are apt to develop into new independent individuals. That these portions are not detached from the parent coral but remain fixed to the skeleton does not take away from the theoretical significance of separation.

KORSCHULT and HEIDER point to the fact that fragmentation is originally not a phenomenon of itself, but the effect of processes of fission or budding.

The processes in *Fungia*, dealt with in this paper are undoubtedly related to budding. Sometimes daughter-individuals are found on the aboral surface of specimens, whose oral surface presents no anomalies. These daughter individuals are true buds. They have the same outward appearance and are attached to the parent-coral in the same way as the buds which were developed experimentally. Daughter-individuals can also be developed from that part of the living tissue of a mother-coral, which is contiguous to a small region of the margin of which the living tissue has been destroyed. The mother-coral will then remain alive, although it is slightly injured, and the young individuals, derived from a portion of the living tissues, are buds also in this case.

The evidence produced shows that any part of the tissue may develop into a complete animal. This, however, occurs only when the interconnection between the living parts of the original animal ceases to exist in consequence of destruction of part of the tissue.

The place where the young individuals develop is very different. They may arise at the top of the costae or between two costae or, when they are larger, on several costae together (Fig. 1). In corals that were inverted while the tissue was being destroyed, young individuals may develop between the septa and in the vicinity of the mouth, i.e. on the oral surface.

<sup>1)</sup> P. DEGENER, Versuch zu einem System der Monogonie im Thierreiche. Zeitschrift f. Wiss. Zoologie. Bd. 113, 1915.

<sup>2)</sup> E. KORSCHULT und K. HEIDER, Lehrbuch der vergleichenden Entwicklungsgeschichte der wirbellosen Thiere. 1 u. 2 Aufl. Allgemeiner Theil. 4 Lief. 2 Hälfte. 1910.

Some of the experimental animals could have survived in a slightly altered form. They are the corals, in which new mouths had been formed round the destroyed central part of the oral surface. Most specimens however had altered their shape completely: the ultimate result would ever have been a defunct disc with a number of young living individuals, chiefly on the under surface and at the margin. The young individuals on the under surface were in unfavourable conditions for further development, although some were already rather large (Fig. 4). The young Fungiae at the marginal regions, would have developed into a stemmed specimen if the corals had remained on the reef. When their disc has grown to a certain size, it falls off and at the upper extremity of the stem a new disc forms. These young Fungiae, originated from the last living residues of a defunct specimen, develop further in the same way as young individuals do, which are generated from fertilized ova.

*Leyden, Jan. 1923.*

*Zoological Laboratory of the University.*

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Plate I



Fig. 1. Part of the margin of the aboral surface of *Fungia fungites* No. 463. Living parts removed. Many small buds and a few larger, less regular ones. Magnified  $\times 5\frac{1}{2}$ .



Fig. 2. Other part of the margin of the aboral surface of the same specimen. Besides a few smaller buds also a large number of irregular elements of the skeleton, especially of the columella of larger buds, are observable. Magnified  $5\frac{1}{2}$ .

The photographs for figs 1 and 2 have been taken by Mr. G. F. J. BLEY of Batutulis near Buitenzorg.

Plate II.

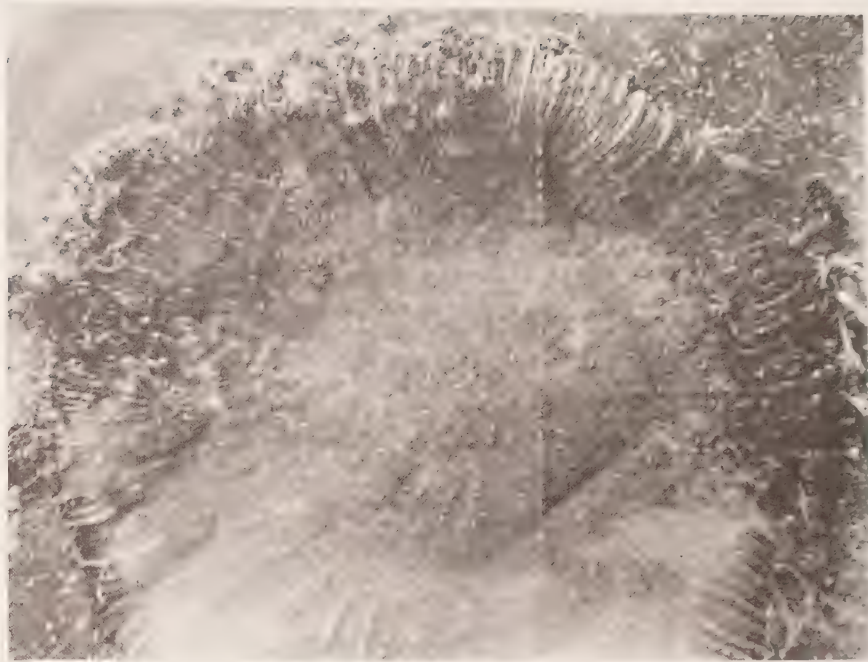


Fig. 3. Lower surface of *Fungia fungites* No. 463 living. A number of large buds, whose living parts are connected with the unaltered tissue of the lower surface. Natural size.

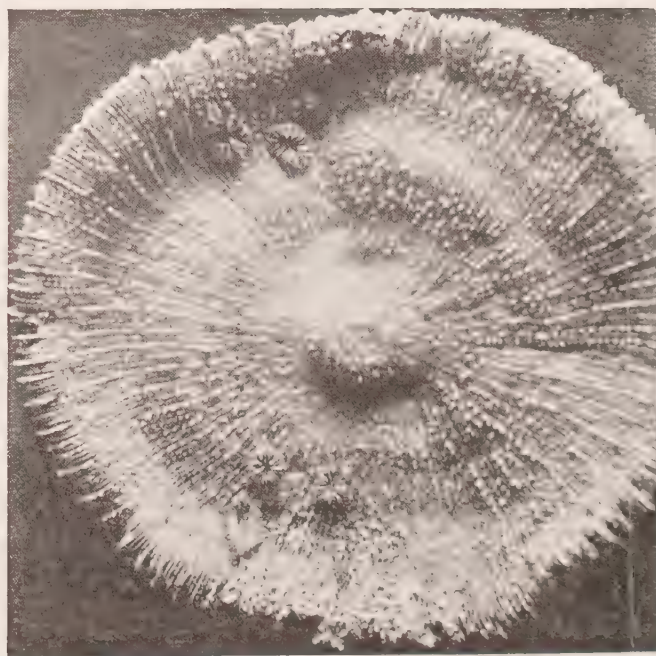


Fig. 4. Lower surface of *Fungia fungites* No. 500. Buds in the living part adjacent to a portion of the margin where the soft parts have died off.  $\frac{3}{4}$  nat. size.

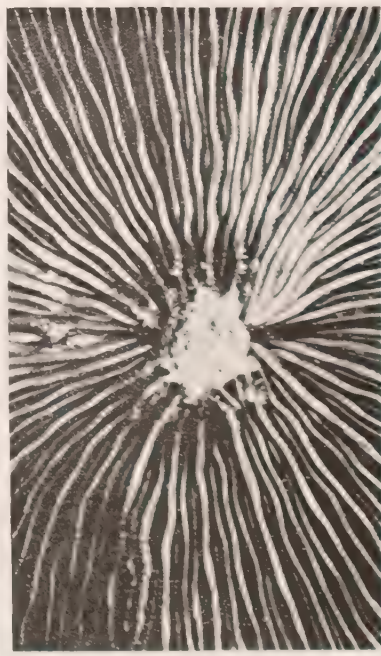


Fig. 5. The central portion of the oral surface of *Fungia fungites* No. 508. By the side of the plug of putty new mouths had been generated, which, towards the central part of the parent-coral, are encircled by raised portions of the old septa with larger dentations.  $\frac{2}{3}$  nat. size.







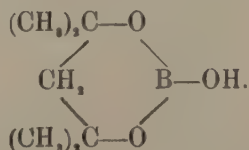
**Chemistry.** — "*The Valency of Boron*". By Prof. J. BÖESEKEN.

(Communicated at the meeting of December 30, 1922).

As the complex organic boric acid compounds have gradually acquired a great significance for the determination of the composition of a number of organic compounds and for the knowledge of the configuration and of the state of motion of the molecules in space, it was felt as a serious deficiency that the existence of these complex compounds had so far been exclusively derived by an indirect way, and that no compound had as yet been separated, the composition of which had been entirely made clear.

Some years ago we had, indeed, succeeded <sup>1)</sup> in obtaining some well crystallized salts of pyrocatechol boric acid, but they seemed to be built up in such a complicated way that no accurate conception could be formed of their composition.

Now it chanced that Mr. HERMANS <sup>2)</sup>, who was engaged in an investigation of the equilibria in the system glycol + acetone  $\geq$  glycol acetone + H<sub>2</sub>O, and also examined the behaviour of the glycols towards boric acid, obtained a compound that crystallized beautifully from tetra-methyl-propane-diol-1.3 and boric acid, which according to analysis and properties possessed the following cyclic composition :



Against our expectation this compound, which had a delicate saffron odour, was hardly acid, at any rate less acid than boric acid itself, as a solution of this substance had a smaller conductivity, while it could be ascertained by determinations of the freezing-point that it had not entirely split up into its components in aqueous solutions.

The discovery of this compound made a renewed investigation of the boro-pyro-catechates necessary.

<sup>1)</sup> Recueil **37**, 184 (1917).

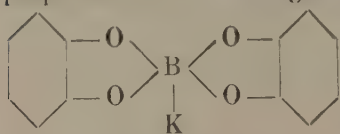
<sup>2)</sup> Cf. These Proc. following communication.

Mr. HERMANS, who undertook this investigation (c.f. following communication) soon succeeded in clearing up the composition of these compounds.

The empirical formula  $\text{KBO}_4(\text{C}_6\text{H}_4)_2$  applies to the beautifully crystallized potassium salt; the volatile ammonium salt is  $\text{NH}_4\text{BO}_4(\text{C}_6\text{H}_4)_2$ , aniline salt  $\text{C}_6\text{H}_5\text{NH}_2\text{HBO}_4(\text{C}_6\text{H}_4)_2$ , from which through careful heating in vacuum, the free acid  $\text{HBO}_4(\text{C}_6\text{H}_4)_2$ , (prepared and analysed by Mr. MEULENHOF) was obtained.

There are, accordingly, two pyrocatechol rests bound to the boron atom, in which an *entirely new type of compounds originates*, as the potassium salt hardly reacts alkalically, and, as has been known for a long time already, the relatively strong acid nature of the hydrogen derivative manifests itself in aqueous solution by increase of the conductivity.

In view of the empirical constitution and this modification of properties the below-given structural formula naturally suggests



itself, in which we must imagine the anion of a relatively strong acid to have arisen through binding of the fourth oxygen atom to the boron. The acid is

partially hydrolysed by water, but can be sublimated undecomposed in anhydrous condition. Also in its spatial structure the anion will be an antipode to the kation of the ammonium compounds; the four O atoms will lie in the four angles of a tetrahedron, and the two benzene rings then are vertical to each other.

The discovery of this type of boron compounds throws light on the composition of a great number of other boron compounds, and indirectly gives a powerful support to the recent considerations on the atomic structure in general. In this connection we must devote a few words to LEWIS<sup>1)</sup> and LANGMUIR's<sup>2)</sup> atomic model, and to the natural system of elements according to KOSSEL<sup>3)</sup>.

Very much simplified and somewhat modified<sup>4)</sup> these hypotheses come to what follows:

The atom is assumed to be a positive nucleus surrounded by different shells of electrons, in which the number of electrons must

<sup>1)</sup> G. N. LEWIS. Journ. Am. Ch. Soc. **38** 762 (1916).

<sup>2)</sup> IRVING LANGMUIR *ibid* **41** 868 (1919) and **42**, 274 (1920).

<sup>3)</sup> Ann. der Physik **49** 229 (1916).

<sup>4)</sup> I wish to state here emphatically that I apply these considerations exclusively to the *first* period of the system, because I consider the atoms of the second period already to be too complicated to satisfy the simple postulates.

be equal to the excess of protons of the nucleus. The electrons which can more or less easily be shifted, and can even be removed, are found in the outer shell, and also electrons of other atoms can penetrate into this outer shell.

There is further a general tendency to gather eight electrons in this outer shell, because this represents most likely a very stable condition of equilibrium. We meet with this constellation in the noble gases, which do not possess chemical affinity. Only helium has only two electrons in its outer shell, and evidently forms an exceedingly stable whole with the nucleus.

The mono-valent metals have only one electron in their outer shell, and will easily split this off, in this way getting into the condition of the nulli-valent element, which stands one place lower down as to its rank; the elements of the seventh group, the halogens, have seven electrons in the outer shell, and will have a tendency to add one electron, passing with it into the condition of the nulli-valent element, which is one place higher in rank.

Thus an exceedingly stable substance of the type of Helium-Neon will be formed when Li and F are joined, with this difference that there exists a very strong electric field between these atoms, which is wanting in the noble gases.

KOSSEL has designated this kind of bonds by the name of *hetero-polar*, they exist between all metallic elements on one side and the non-metallic ones on the other side. When the electron of the metal has entered the shell of the non-metal, this has obtained for the metal-ion a same value as the seven already present ones, which means that the metal-ion is no longer bound to a definite place in the molecule; it can place itself opposite to each of the electrons present.

When the number of electrons in the outer shell increases, resp. decreases, they no longer get so easily quite outside, resp. the power to absorb foreign electrons has diminished; then ensues an interpenetration of the two shells, in which one electron of each of the atoms joins to a pair in the mutual shell division.

This is the *homöopolar* bond according to KOSSEL, in which the two atoms are bound to a very definite place. The hetero-polar or briefly *polar* bond gives rise to molecules which conduct the electric current e.g. in aqueous solution; the homöo- or *non-polar* bond is met with in substances that do not conduct the electric current.

As a type of the first we may name the alkali-halogenides, as a type of the second the organic compounds, but also water, boron-trichloride etc.

In the polar bond the atoms are thought separated, in the non-polar bond they penetrate into each other at definite places.

There is still a third kind of bond, which comes near to the

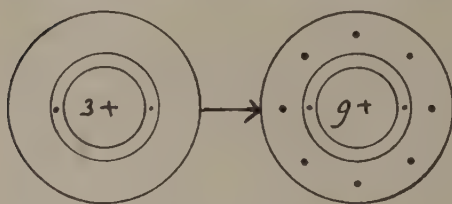


Fig. 1a.  
Lithium fluoride.

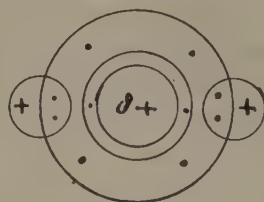


Fig. 1b.  
Water.

non-polar bond, and is distinguished from it only in form, not in nature.

It is seen from the symbol for water that the oxygen atom has still two pair of electrons in the outer shell. These endow this molecule with the power to combine with other molecules, and especially with those of which one of the atoms lacks a few electrons in the outer shell.

Thus we must imagine that metal atoms which have ceded their electrons to acid rests on the salt formation, can get saturated with water molecules, and thus form hydrated metal ions. This kind of non-polar bond is that which was supposed to come about through by-valencies, and which is explained from the tendency to collect eight (or sometimes more) electrons in the outer shell.

It is easy to see that ammonia, though a saturated compound, can combine with a great number of substances owing to the free electrons in the outer shell. All these bonds are of quite the same nature as those that come about through the principal valencies. The penetration of these ammonia molecules into the metal atom often gives it a more pronounced electro-positive character.

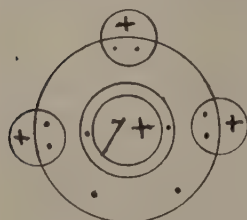


Fig. 2.  
Ammonia.

That this bond is really restricted to a definite place of the molecule, follows from MEISENHEIMER's investigation <sup>1)</sup>, in which he has succeeded in splitting up methyl ethyl aniline oxide into its optical antipodes. The four non-polar bonds, among which that where the nitrogen with its free electrons, has penetrated into the outer shell of the oxygen find a place in the angles of a tetrahedron.

<sup>1)</sup> Berichte 41, 3967 (1908).



We point out that the nitrogen here behaves as a tetra-valent substance, the oxygen as a univalent one.

Ammonia, in spite of its having 8 electrons in its outer shell,

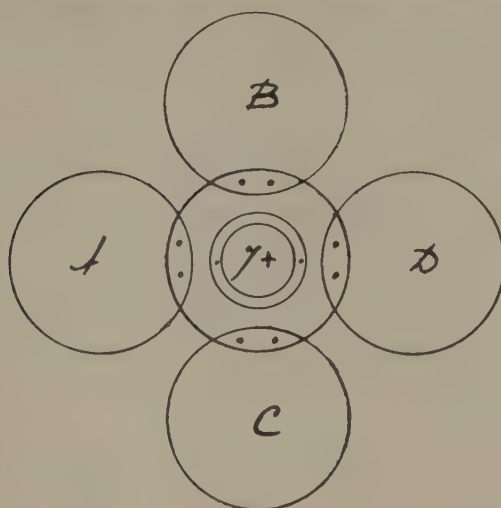


Fig. 3.

A = phenyl, B = methyl, C = ethyl, D = oxygen.

Methyl ethyl phenyl ammonium oxide.

can bind certain definite other atoms non-polarly, provided there be also an atom present that the electron, which is now in excess (and is, therefore, expelled) can take up.

This may also be expressed as follows: ammonia passes into the positive ion condition when forming a bond with a hydrogen atom, or in other words: ammonia can only receive a hydrogen *ion*, as it is saturated with electrons. Here the nitrogen does not become tetra-valent, but penta-valent. This fifth valency, however, has another character: it gives rise to a polar bond.

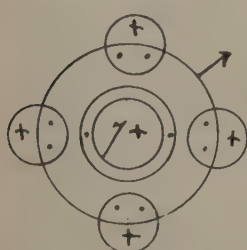


Fig. 4.

Ammoniumion.

It is this very power through which a number of atoms, which to start with, have an electro-negative character, acquire the property of an alkali-metal; we need only mention iodine and sulphur.

We may now apply these considerations to the boron atom, and examine in the first place what is the nature of the bonds in the simple derivatives of this element. The halogen compounds are the most suitable to decide this question.

These have  $BX_3$  as constitution and entirely possess the character of acid chlorides, and not of salts. The three electrons are, accordingly, not ceded, as even the fluorine atoms are non-polarly bound.

In these compounds boron has only six electrons in the outer shell; in some respects they will, therefore, have an unsaturated character (Fig. 5). These halogen compounds can, indeed, become saturated in two ways.

The *first* way, which has been known longest and has already been explained by WERNER to a certain extent, refers to the adoption of a molecule HF. Then there is formed e.g.  $HBF_4$ , a mono-basic acid. It may now be assumed that a fourth atom F becomes non-polarly bound, which, however, is not possible, as boron has no free electron left, unless at the same time an electron (of the H) is taken up, and consequently the group  $BF_4$  passes into the negative ion-condition (Fig. 6).

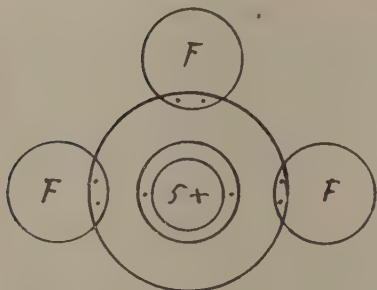


Fig. 5.

Borium fluoride.

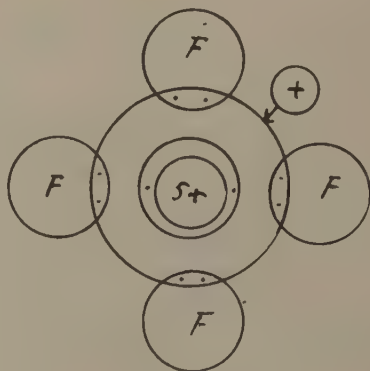


Fig. 6.

Borium fluor hydrogenic acid.

It may also be said that the polarly-bound HF-molecule enters the shell of the boron with two of the electrons of the fluorine atom, the whole  $BF_4$ -group becoming a negative ion.

For the H-ion it is entirely immaterial whether the ceded electron is attached to one of the four fluorine-atoms outside or inside the shell of the boron; as ion it has no fixed place in the molecule, and can wander all round the complex.

In view of the mono-valency of fluorine and of the complex, boron may be assumed to be penta-valent with as much reason as the nitrogen in ammonium compounds.

The *second* way in which boron fluoride can add to its electrons is: to combine with molecules of which there are two electrons

available in the outer shell of one of their atoms, without this giving necessarily rise to ionisation.

Thus  $\text{BF}_3$  forms stable compounds with  $\text{PB}_3$  and with ammonia,

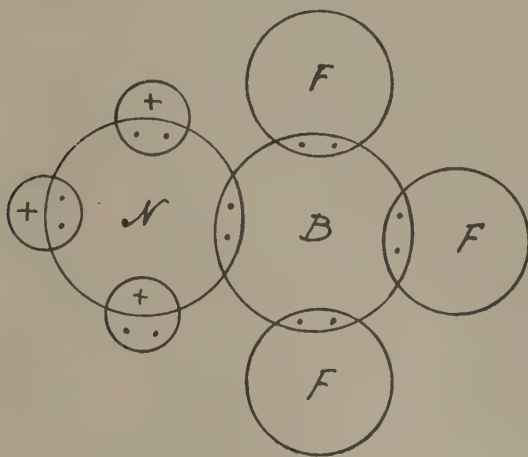


Fig. 7.  
Boron fluoride ammonia.

of which the latter can be distilled undecomposed. Their constitution may be represented by the above simplified symbol; the two electrons which the N of the ammonia has in excess have penetrated into the shell of the sphere of the boron, thus forming a non-polar bond. Both atoms have eight electrons in this shell, and are mutually saturated (Fig. 7).

It is not subject to doubt that when different groups are substituted for the H-atoms at the N, a substance is formed which can be split up into its optical antipodes<sup>1)</sup>.

As regards the valency of the boron, this may be put, like that of the nitrogen, at four, as there is no reason to assume the bond between the N and the B to be of another nature than between the B and the F (resp. between the N and the H).

Let us now proceed to the complex boric acid compounds. The very weak, volatile boric acid itself is, at least for the greater part, a derivative of the tri-valent boron, in which all the bonds are non-polar. In aqueous solution a very small part will be a derivative

<sup>1)</sup> It may cursorily be pointed out that the constitution of the addition products of  $\text{AlCl}_3$  with a number of organic and inorganic compounds can be seen in entirely the same light.

of the penta-valent boron, in which one of the bonds is polar (see further).

The non-acid complexes agree with this, the acid ones, which are formed with the poly-hydroxy compounds, the hydroxyl groups

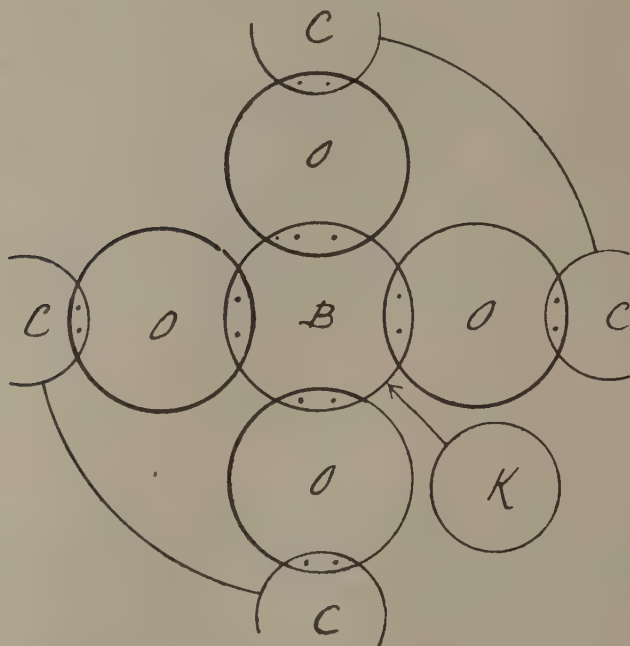


Fig. 9.

Potassium boro pyro catechate.

of which have a favourable position, are derivatives of the penta-valent element. Let us choose as an example potassium boro pyro catechate.

The four oxygen atoms of the two pyro catechol rests are bound to the boron atom. This cannot take place, however, until one electron of a metal or of an H-atom has been ceded to the complex. When this has once been accomplished, it is immaterial for the potassium (or H-) atom, where this electron is to be found in the complex; in view of the tetra-valency of the carbon, of the bi-valency of the oxygen, and of the mono-valency of the complex, the boron may here be assumed as penta-valent; one of these bonds is then polar (Fig. 9).

The four non-polar bonds, just as in the carbon atom — will be grouped as a tetrahedron, so that we may already expect optical activity in mono-derivatives of the pyro-catechol. These complex



boric acid compounds always being more or less hydrolized in aqueous solution, the splitting up into optical antipodes will be difficult.

In general the negative ion will be particularly easily formed:

1. When the hydroxyl groups of the poly-alcohols have a favourable situation.
2. When the organic rests bear an electro-negative character.
3. When the other atom easily cedes an electron.

1. The researches on the complex boric acid compounds of the last ten years have proved that the substances with a pronounced acid character from scarcely acid compounds are formed particularly easily, when the hydroxyl groups are situated in one plane with the C-atoms bound to them. It may be assumed that the first phase will be the formation of the derivative of the tri-valent boron. When this complex meets a second molecule of the organic compound, the unsaturateness of the boron will collaborate with the favourable constellation of the poly-alcohol to form the very stable derivative of the penta-valent boron.

2. When this favourable situation of the hydroxyl groups coincides with strongly electro-negative properties of the poly-oxy-compounds, as of  $\alpha$ -hydroxy acids and aromatic ortho-hydroxy-acids, these penta-valent boric acid compounds will be exceedingly easily formed. Mr. HERMANS has actually succeeded (cf. following communication) in proving this for boro di-citric acid, and in ascertaining the constitution of the already known boro di-salicylic acid zinc from this point of view.

3. It was to be expected that especially the alkali-salts of these complex acids could be isolated, because the complexes are only realizable on adoption of an electron, and this is easily ceded by an alkali-metal. We meet here with the same influence which the metal atom in general exerts on the stability of the acid rest, which renders it possible to obtain salts of which the corresponding acid is unstable and even unknown.

This latter circumstance renders it also desirable to write the metal atom by the side of the atom to which it has ceded the electron, though in reality the whole complex becomes a charge richer, and it therefore seems indifferent to a certain extent where this metal atom is placed, since as an ion it is not bound to a definite place <sup>1)</sup>.

<sup>1)</sup> That this is not quite immaterial may appear from the different behaviour of  $\text{AgNO}_3$  and  $\text{KNO}_3$  resp.  $\text{AgCN}$  and  $\text{KCN}$  towards alkyl iodides, which will be discussed later.

We are now able to bring some order in the inorganic derivatives of boron.

The volatile boric acid and its esters are, as was stated above, derivatives of tri-valent boron, and as such, somewhat unsaturated. It will try to supply the deficiency by complex formation.

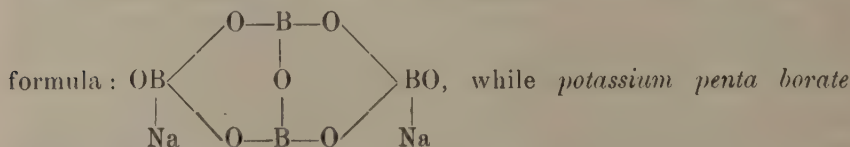
AUERBACH'S investigations <sup>1)</sup> have brought to light that when an insufficient quantity of a base is distributed between boric acid and arsenic acid there is formed far more borate than was to be expected according to the dissociation constant of boric acid. Complexes must be formed which are much more strongly acid than boric acid in diluted aqueous solution.

Hence in virtue of 3 the added bases cause the quantity of poly-boric acid ion to increase.

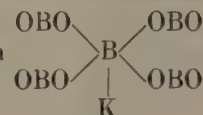
This is corroborated by an investigation of P. MÜLLER <sup>2)</sup>, who could shake out but very little boric acid from a mixture of borate and boric acid with amyl alcohol, though the free acid is easily dissolved in it, evidently because the boric acid was bound with formation of poly-borates in consequence of the above-mentioned kation-action.

These stronger poly-boric acids will be derivatives of penta-valent boron, and accordingly in the symbol a place may be assigned to the metal atoms which promote this phenomenon, next to the boron atom.

The *metaborates* then have the composition  $M(BO_2)_n$ , *borax* has the



$KB_5O_8$  (see HERMANS, following communication), which crystallizes

beautifully from formic acid, possesses the constitution 

all assumed to be anhydrous.

There are described a great number of poly-borates; on the condition that the number of penta-valent boron atoms be taken the same as the number of positive metal valencies, their configuration can be easily constructed.

*Boric acid anhydride* is distinguished from boric acid by its slight

<sup>1)</sup> Zeitschr. anorg. Ch. 37 353.

<sup>2)</sup> ABEGG Handbuch III. 1 p. 32 (1905).

volatility; this furnishes a sufficient ground for assuming this substance to be strongly polymerized. This may possibly be explained from the tendency of the boron atoms of one molecule to form non-polar bonds with pairs of electrons of the oxygen atoms of other molecules. It is possible to form an idea of this polymer by imagining the anhydride molecules to be built up in column, in which alternately the oxygen atoms have penetrated into the outer shells of the boron atoms, thus contributing to the completion of the "octet". There are enough free atoms left at the oxygen atoms to render the easy hydration to boric acid comprehensible.

*The boro hydrogen compounds.* From the place of the boron in the system it was to be expected that the affinity of the H should be slight. The interesting investigations by Stock and his pupils<sup>1)</sup> have really proved that these compounds are formed in very small quantities from magnesium boride, and are very unstable. At first  $B_2H_6$  and  $B_4H_{10}$  were separated as gaseous boro-hydrogens, and later  $B_5H_9$  besides higher boro-hydrogens. Stock is of opinion that the boron must be assumed to be tetra-valent in these compounds.

He, therefore, tried to prepare halogen boron compounds  $BX_4$ , in which he did not succeed, which is, indeed, not astonishing in view of what precedes; such a combination can only be realized when at the same time an electron is added.

The  $B_2H_6$  obtained by him is not necessarily a derivative of tetra-valent boron; the  $BH_3$ , which would have to be formed in virtue of the tri-valency of the boron, is evidently so unstable that two molecules inter-penetrate, in which, however, one of the B-atoms must more or less change into the ion-condition. It is actually immediately adopted by KOH with formation of  $KBOH_3$  (probably a mixture or combination of  $KBOH_2$  and  $KBOH_4$ ) and  $H_2$ . Accordingly it is a compound with tri- and penta-valent boron, which through this makes the impression of being a derivative of the tetra-valent element (see the symbol on the following page).

Nor need the second gaseous boro-hydrogen  $B_4H_{10}$  possess a tetra-valent boron. In this two  $BH_3$ -groups can be bound to each other, each of them bearing a  $BH_3$ -group, while besides two H-atoms have passed into the kation-condition, and the rest, therefore, forms a bi-valent anion. The  $B_5H_9$ , which is, moreover, the most stable boro-hydrogen<sup>2)</sup>, can certainly, not consist exclusively of tetra-valent boron atoms. If it is assumed that one of the boron atoms is bound

<sup>1)</sup> Berichte **54** A 142—158 (1921).

<sup>2)</sup> Berichte **54** A 155 (1922).

to four  $\text{BH}_2$ -groups, which at the same time has taken up an electron with H-nucleus, the relative stability and the fact that this borohydrogen dissolves in KOH without residue, evidently with formation of a salt, has been explained in a satisfactory way. Its formula is, therefore,  $\text{H}[\text{B}(\text{BH}_2)_4]$  with one penta-valent and four tri-valent boron atoms.

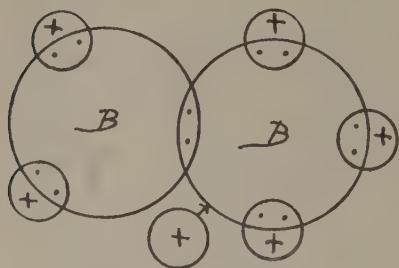


Fig. 10. Borohydrogen.

In the boro-alkyl compounds transition of an H-atom into the ion-condition is not possible:  $\text{B}(\text{CH}_3)_3$  has been separated, and a polymerisation to  $[\text{B}(\text{CH}_3)_3]_n$  has not been observed — also boro-triphenyl was lately prepared.

That the boro-alkyl compounds can combine with ammonia<sup>1)</sup> can be explained in entirely the same way as for  $\text{BF}_3$  (cf. p. 103), there is sufficient reason in these non-polarly bound molecules to assume the boron, just as the nitrogen, to be tetra-valent.

*Boro-nitrogen.* BN. It has not been possible so far to melt, this substance, which forms a white powder and which is very resistant against the action of the air also at high temperature, for which reasons it has been proposed as material for fire proof receptacles; it is very interesting as far as the considerations given here are concerned. In appearance the demand of the valency has been completely fulfilled, as the tri-valent nitrogen is combined with the tri-valent boron. When, however, the properties of nitrogen compounds of other light elements, as cyanogen gas, halogen nitrogen compounds, etc. are considered, boro-nitrogen must at any rate be assumed to be very far polymerized.

When every nitrogen atom is supposed to be surrounded by three boron atoms, and these again each bound to three nitrogen atoms and so on, two electrons of every nitrogen atom remain available in the outer shell for a non-polar bond. Inversely every boron atom can be joined by a pair of electrons. This mutual saturation is here exceedingly probable, because then at the same time an exceptionally stable structure can be attained, viz. that of the carbon in diamond. The properties of boron nitrogen lead us at any rate to expect

<sup>1)</sup> Berichte 54 B 531 (1922). The ammonia compound of boro-trimethyl is a volatile well-crystallizing compound, much more stable when exposed to the air than  $\text{B}(\text{CH}_3)_3$  itself.



a very stable configuration. If attempts to bring it to crystallisation should succeed, a substance may be expected with a very high refractivity and very great hardness, and with a still more considerable resistance against external influences than any amorphous product known so far.

The difference with the way of binding of the carbon in diamond is this that one of the bonds at the moment of its formation is not quite equal to the other; when one considers, however, that this difference has vanished after the two elements have combined, so that it is impossible to decide which of the four was this particular bond, the expectation is the more justified that crystallized boron-nitrogen will have the character of diamond.

It is seen that when represented in this way, the idea of the valency begins to diffuse. The boron is more than tri-valent with respect to the nitrogen, because the element lacks something. And the nitrogen is more than tri-valent with regard to the boron, because in the simple compound this element has something too much. Combined they make, therefore, the impression of two tetra-valent elements. Hence the valency is replaced by WERNER'S coordination value, to which a firmer foundation is given by these considerations.

If it should appear, e. g. from the Röntgenogram, that the diamond structure is applicable to the crystallized boron-nitrogen, this proves at the same time that a distinction between principal- and by-valencies is not rational, and that polar and non-polar bonds should be substituted for this, in which the non-polar bond is a connection between two atoms, which in consequence of mutual repulsion of some such bonds, has taken up a certain place in the molecule, whereas the polar bond forms a connection between one of the atoms and a rest, which will often consist of a multiple of atoms, but which, also when it consists of only one atom, is not fixed to a definite place of it.

It is self-evident that in the first periods, in which the atoms are simply composed, the number of pairs of electrons will not be greater than four, and the coordination-value will not exceed this number.

As the atoms get more complicated, the coordination-value can also increase; we see this already happen in the second period in aluminium, many compounds of which are known, in which this element is bound non-polarly to six atoms.

With regard to the other boron compounds, I will still draw attention to additional compounds of the boric acid esters with

alcoholates, e. g.  $\text{Na}[\text{B}(\text{OCH}_3)_4]$ , which entirely possess the character of salts in absolutely alcoholic solution — they are decomposed by water.

The boron is non-polarly bound to the four mono-valent  $\text{OCH}_3$ -groups, which is only possible through the complex having taken up one electron.

A very interesting group of compounds has been found by W. DILTHEY<sup>1)</sup>. He found that when acetyl acetone-rests had substituted two chlorine-atoms in  $\text{BCl}_3$ , the third chlorine atom assumed the character of an anion, hence the rest of a kation. He rightly calls these substances *boronium compounds*: the considerations developed

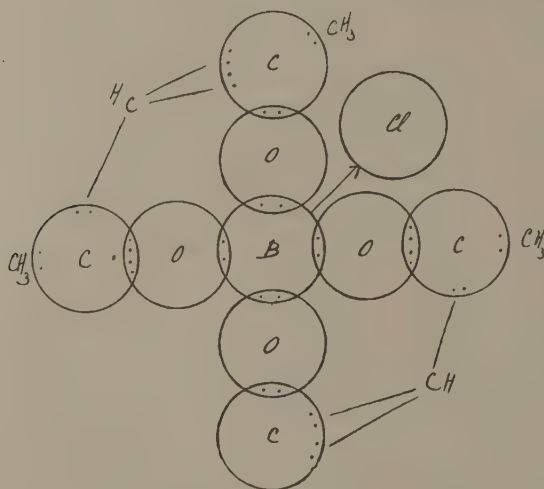


Fig. 11.

Boron di-acetyl acetone chloride.

above account satisfactorily for the phenomenon. The two acetyl acetone rests have as enol replaced two of the chlorine atoms of  $\text{BCl}_3$ , and then are bound non-polarly to the boron atom. The favourable situation of the  $\text{C}=\text{O}$ -groups with regard to the boron-atom now gives rise to the penetration of two electrons of each of the oxygen atoms into the outer shell of the boron, causing non-polar bonds; this is, however, only possible, when at the same time the third chlorine atom, which was at first non-polarly bound, passes into the (polarly-bound) anion state and the boron complex becomes a kation.

<sup>1)</sup> Annalen 433, 300 (1906).

There is certainly no need to state explicitly that only a sketch has been given in the above. It seemed, however, desirable to me to test KOSSEL's and LEWIS-LANGMUIR's hypotheses by the simplest atom that can be bound both polarly and non-polarly to other atoms, for it is to be expected here that the complex compounds will be built up in the least complicated way.

Complications occur in the elements of the second period, e. g. Al, Si, and S, as appears from the existence of compounds as  $\text{Na}_3\text{AlF}_6$ ,  $\text{K}_2\text{SiF}_6$  and the derivatives of the hexa-valent sulphur. In connection with the above it would have to be assumed that these atoms try to bring together *six* pairs of electrons in their outer shell, which then possibly might have to be ascribed to the influence of the electrons of the first spherical shell on those of the second. Before this can be examined more closely, the phenomena referring to the simplest elements will first have to be more fully cleared up.

In the case of boron it is, indeed clear, that as regards the formation of compounds *pairs* of electrons play an important part, and that especially the non-polar bond, i. e. the bond that does not conduct electrically, is brought about by such pairs. If it is further borne in mind that the latter kind of bonds is much less reactive than the former, it is natural to suppose that the difference between polar and non-polar bond consists in a greater closeness of the latter. The non-polar bond might be compared to an electro-magnet with a well-closed armature or a toroid, whereas in the polar bond the armature is removed or the toroid opened.

A similar image might be applied to the action of catalysts, in which it is likewise assumed that closed bonds are opened, which gives rise to a greater chance of interaction when meeting other molecules.

*Delft*, Dec. 1922.

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**Physics.** — “*On the diffraction of Röntgen-rays in liquids*”. II.

By Prof. W. H. KEESOM and Prof. J. DE SMEDT. (Communication N°. 12 from the Laboratory of Physics and Physical Chemistry of the Veterinary College). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of January 27, 1923).

§ 1. *Introduction.* The experiments on the diffraction of Röntgen-rays described in Comm. N°. 10<sup>1)</sup> were all made with  $K_{\alpha}$ -rays of copper. No diffraction ring was observed caused by the interference of rays scattered by the separate atoms in the molecules. F.i. in the case of oxygen this might be ascribed to the circumstance, that the distance of the centres of the systems of electrons grouped round the atom nuclei is too small to give an interference ring with rays of that wave length (viz. smaller than  $0.95 \text{ \AA}$  for  $\lambda = 1.54 \text{ \AA}$ ). Therefore it seemed desirable to repeat some of the experiments with rays of a shorter wave length.

We have now made several observations with  $K_{\alpha}$ -rays of molybdenum ( $\lambda = 0.71 \text{ \AA}$ ).

§ 2. For method and apparatus see Comm. N°. 10. The rays emitted by the molybdenum anticathode were filtered by  $0.35 \text{ mm.}$  zirconium.

§ 3. *Results of the observations on the principal diffraction ring.* We now exposed liquid oxygen, argon and nitrogen, also water and carbonic disulphide.

For oxygen, argon, water and nitrogen (investigated for the first time now) we found confirmed that the principal ring is due to neighbouring molecules, which we may consider to be distributed approximately as spheres packed together as closely as possible and filling up the space occupied by the liquid.

This time we obtained a diffraction ring for carbonic disulphide

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<sup>1)</sup> These Proceedings 25, 1922, p. 118.



too and this gave a deviating value for the distance between the diffracting particles. This is evident from the following table. Here  $\varphi$  is again the half top angle of the cone formed by the diffracted Röntgen rays.  $M$  and  $d$  have been written for the molecular weight and density, while

$$a = \frac{7,72 \lambda}{4\pi \sin \frac{\varphi}{2}}$$

denotes the distance between the diffracting particles. Here we again have made the assumption that the observed diffraction ring is due to the cooperation of arbitrarily orientated systems each of two particles at that distance from each other.

TABLE I.				
Substance		$\varphi$ ( $\lambda = 0.71 \text{ \AA}$ )	$a$	$1.33 \sqrt[3]{\frac{M}{d}}$
Oxygen	(9 plates)	12.50°	4.0 $\text{\AA}$	4.0 $\text{\AA}$
Argon	(1 plate)	13.0	3.85	4.1
Water	(1 " )	13.44	3.73	3.6
Nitrogen	(1 " )	11.34	4.42	4.4
Carb. disulph.	(1 " )	13.23	3.8	5.2

Instead of formulating a special hypothesis on the deviating behaviour of  $\text{CS}_2$ , we prefer to postpone this until more substances showing a similar deviation have been investigated.

The diffraction rings obtained now are sharper than the former ones, the liquids being radiated this time in a tube of 1 mm. diameter.

§ 4. *Results of the observations on the second ring.* On six plates of oxygen and on those of argon and nitrogen the second ring is distinctly measurable. The other plates do not show this ring, probably because the obtained films are less blackened. For argon too this ring is very weak.

TABLE II.		
	$\varphi$	$a$
Oxygen	19.5°	2.57 Å
Argon	18.9	2.65
Nitrogen	17.0	2.95

These values of  $a$  show a striking agreement with the values obtained in Comm. N°. 6a<sup>1)</sup> for the diameter of the molecule<sup>2)</sup> viz. for oxygen  $\sigma = 2.65$  Å, for nitrogen  $\sigma = 2.98$  Å. This supports the assumption made in Comm. N°. 10 that this diffraction ring should be due to the collaboration of two molecules touching each other.

With this wave length we also found for water at the outside of the principal ring a rather uniform blackening, rather sharply bounded at  $\varphi = 24^\circ$ , which corresponds with a distance  $a = 2.1$  Å.

§ 5. *For oxygen and nitrogen no diffraction by separate atoms in the molecule.* On a well blackened film of oxygen and on that of argon we found indications of a third maximum of blackening, for oxygen at  $\varphi = 29^\circ$  and for argon at  $\varphi = 30.5^\circ$ . We do not pretend the existence of this third maximum to be doubtlessly fixed by these indications. We only draw the following conclusion: If this third maximum really exists, it also does so for argon, so that this maximum cannot be ascribed to the interference of rays that are scattered by the separate atoms in the molecules.

Though on several films the principal diffraction ring is blackened very intensively, no trace of an interference figure of the separate atoms in the molecule was found in these experiments. Yet with the here used wave length a diffraction ring would have been obtained for a distance of the diffracting particles greater than 0,43 Å<sup>3)</sup>.

For a partial verification of the above we made still an exposition

<sup>1)</sup> These Proceedings 23, 1920, p. 939.

<sup>2)</sup> In fact the smallest distance that is possible between the centres of two molecules in the gas.

<sup>3)</sup> According to the discussion of the band spectra the distances of the atom nuclei would be for oxygen and nitrogen resp. 0,85 and 1,12 Å: A. EUCKEN, Z.S. f. Elektrochemie 26, p. 377, 1920. Comp. W. LENZ, Verh. D. physik. Ges. 21, p. 632, 1919.

with Cu-K $\alpha$  rays (9 mA,  $\pm$  25 KV). Though this film is thoroughly blackened, only two rings have been obtained.

It may be suggested, that the rings obtained in these experiments are all due to atoms that temporarily are arranged in a crystal lattice. The values for the diameters of these rings found in this Comm. exclude a cubical arrangement<sup>1)</sup>. The data are not sufficient to know, whether those temporary arrangements might belong to a crystal structure from an other class of symmetry<sup>2)</sup>. Meanwhile the fact that freezing takes place suddenly at a definite temperature and the possibility of undercooling do not seem to point in the direction of such temporary crystal arrangements.

Lead by these considerations we have made still a plate of water at  $\pm 0,5^\circ$  C. The obtained interference figure perfectly agreed with that found at room temperature. At the outward side of the nearly uniform blackening only the intensity proved to be somewhat greater. In this way a second ring develops itself there, an indication of the presence of more double molecules at those low temperatures. No indication was found of the presence of more or greater crystal groups.

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<sup>1)</sup> Comp. Comm. N<sup>o</sup>. 10 p. 122, footnote 1.

<sup>2)</sup> Nitrogen and argon crystallise cubically: W. WAHL, Proc. Roy. Soc. A 87, p. 371, 1912; oxygen below the melting point first hexagonally: W. WAHL, Proc. Roy. Soc. A 88, p. 61, 1913.

**Bacteriology.** — "*On the Bacteriophage and the Self-purification of Water*", by Prof. P. C. FLU.

(Communicated at the meeting of Dec. 30, 1922).

In 1896 HANKIN<sup>1)</sup> reported that the water of various rivers in India, i. a. the Yumna and the Ganges possesses the property of rapidly destroying cholera-vibriones. He was disposed to ascribe this property to a volatile substance, which he assumed to occur in the water of the said rivers.

Subsequent experimenters have demonstrated that all so-called surface-waters have the faculty of exterminating microbes, notably fortuitous pathogenic germs, at a rate depending on the nature of the water and the temperature of the environment.

EMMERICH, who studied this phenomenon, the so-called self-purification of water, believed that in this process the part of germicide must be assigned to protozoa (Rhizopods, Flagellates and Ciliates) which occur in every surface-water. This view was adhered to by nearly all inquirers, who had occupied themselves with the phenomenon.

D'HÉRELLE refers in his work "*Le bactériophage, son rôle dans l'immunité*" to the phenomenon observed by HANKIN which he thoroughly believes to be merely the effect of a bacteriophage present in the water.

Now, we know that bacteriophages are inactivated at a temperature above 75° C., and that HANKIN could heat water of the said rivers in a closed vessel (a sealed-up glass tube) for half an hour up to 115° C, without depriving it of its bactericidal capacity. We also know that, on heating up the Yumna, and the Ganges-water during the same interval and up to the same temperature (but in an open vessel), it really lost its bactericidal capacity.

Now, in view of these facts it will be difficult to side with D'HÉRELLE, although we must admit at the same time that protozoal action does not explain the phenomenon any better.

Still, it cannot be denied that after D'HÉRELLE's significant discovery and after the establishment of the presence of bacteriophages attacking various germs in all sorts of surface-waters, in seawater and even in the effluent from septic-tanks and from oxidation-beds,

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<sup>1)</sup> Annales de l'Institut PASTEUR Vol. X pag. 175 and 511.



an interpretation of the self-purification of water can hardly be afforded without reckoning with the bacteriophage.

If a special inquiry in this direction were to show that bacteriophages play a more prominent part in the process of self-purification than has hitherto been assumed, we should not only have to revise and modify our conceptions of and our insight into this self-purification of water and our views concerning the action of sand-filters and oxidation-beds, but also a broad field would be opened up for studying the biological cleansing of sewage.

Like many others I also became convinced by my experimentation in India of the prominent part played by protozoa in the destruction of micro-organisms in the surface-water.

For this reason I deemed it a matter of importance to ascertain:

*a.* whether in surface-water, e. g. that in and about Leyden, bacteriophage could be found, and whether the self-purification of that water was in any way due to bacteriophages that might occur in it.

*b.* whether in surface-water, polluted intentionally with a profusion of pathogenic micro-organisms, and allowed, to purify itself, bacteriophages are to be observed that may have annihilated the germs.

*c.* the influence which is played on the purification by substances that kill the protozoa but do not injure the bacteriophages.

*d.* whether protozoa and bacteriophages combined may accelerate the process of self-purification.

To this end the following experiments were performed:

On the 2<sup>d</sup> of June 100 c.c. of various samples of Leyden water were mixed every time with a concentrated broth. The mixture stood during 24 hours at 37° C. and was then filtered first through rock-meal and subsequently through a "bougie". The filtrate was mixed in quantities of 0,5; 0,2; 0,1; and 0,05 c.c. with broth, which was afterwards inoculated with an 18-hour-old Flexner-culture. For an examination for bacteriophage a smear-culture was made on agartubes of the broth thus prepared. After an incubation of 24 hours at 37° C. an estimation was made for "phages".

The result is that from the examined waters bacteriophages can be isolated that react especially to Flexner but also have an action on other intestinal bacteria.

Thus the isolated bacteriophages annihilate all the Flexner, Y, and Shiga Kruse stocks of our collection.

They also have an action on bacillus faecalis alcaligenes, on a proteus and a proteus X 19, but do not act upon Typhus, Paratyphus A. and B. or Enteridite Gärtner, neither on two coli-stocks of our collection.

Neither was any effect of the bacteriophages on cholera-vibrones at all apparent.

This result could be expected, as it is known that from the dejecta of fowls and horses a nearly always highly active bacteriophage antibacteria dysenteriae can be isolated and the surface-water in and about Leyden is being constantly polluted on a large scale by the excrements of a number of living beings, also by those of horses and fowls.

Anyhow this inquiry teaches us that bacteriophage occurs in the surface-water of Leyden.

On the 2<sup>d</sup> of June quantities of 5 Liters of various kinds of Leydenwater were infected every time with two loopfuls of a 24-hour-old cholera-culture. The infected water was placed in large glass receptacles in diffuse daylight at room temperature (15° C.).

On the 21<sup>st</sup> of June we examined two quanta of 25 c.c. of water; in neither of those samples could cholera-vibrones be detected.

Of every sample of 5 L. 25 c.c. was examined for bacteriophages by mixing the water with  $\frac{1}{10}$  of the volume of concentrated broth, and inoculating the mixture with a loopful of an 18-hour-old cholera-culture.

After an incubation of 24 hours at 37° C. the sample was examined in the usual way for bacteriophage anticholera-vibrones. The result was negative.

On the 24<sup>th</sup> of June three flasks were filled each with 0,5 L. of Rijnwater, in which, as our examination had proved, bacteriophage antibacteria dysenteriae was present.

Flask I was inoculated with the whole cholera-culture of a sloped agar tube; flask II in the same manner with typhus-bacilli; and flask III with Shiga-Kruse bacilli.

The fluid of each of the three flasks became very turbid and was placed at room-temperature in diffuse daylight.

On the fifth of July the fluid of each of the three flasks became lucid and was examined for bacteriophage in the ordinary way. In all the flasks we found bacteriophage antidysenteriae, which was present in the water already before the beginning of the experiment, but in the typhus-flask not any bacteriophage antityphus was found, no more than bacteriophage anticholera in the cholera-flask.

The flask infected with Shiga did not become lucid sooner than the one infected with typhus and cholera, which might have been

expected if a protozoal action had been assisted by the bacteriophage antidyenteriae present in the water.

In each flask the number of protozoa increased already two days after the inoculation with the mass of bacteria. Their number was greatest one day before the contents of the flasks became lucid, whereas it decreased after the clarification had been completed; some of them were transformed into cysts.

Again a culture, equal to the one at the beginning of the experiment was transplanted into the flasks in which the typhus-bacteria and the cholera-vibriones had disappeared. The same was repeated twice when, after about ten days the contents had clarified again.

After each new infection the number of protozoa was augmented, as with the first, reached its maximum shortly before the clarification and decreased again after it. Every time a portion of the protozoa were seen to turn into cysts.

When the contents of the flasks had become quite clear again after the fourth infection, another examination was performed for bacteriophage antityphus abdominalis and anticholera vibriones. The result was absolutely negative.

So these experiments go to show that large crowds of typhus-bacteria and cholera-vibriones may disappear without any interference whatever of bacteriophages, from water into which they were introduced fortuitously or intentionally. Even in water containing a bacteriophage anti-bacteria-dysenteriae the *B. dysenteriae* do not disappear quicker than other bacteria not attacked by bacteriophage.

It was nevertheless of interest to examine especially the influence of the presence or the absence of bacteriophage anti-shiga on the rate of disappearance of *B. dysenteriae* from the water.

Two series of experiments were accordingly carried out.

In the first series the fate of *B. dysenteriae* in unfiltered water was compared with that of the same bacilli in filtered water.

Protozoa cannot pass through a filter impervious to bacteria, whereas the bacteriophage is let through.

In the second series a comparison was made of the rapidity of the selfpurification process of bacteriophage containing water that was or was not mixed with KCN.

The results of these tests, which were every time the same, are reported below.

Vlietwater, which contains bacteriophage, was used for the inquiry. Part of it was filtered through a Berkefeld-filter. A control-experiment showed that this water is free from bacteria and protozoa.

Part of the filtered, as well as the unfiltered water was infected

with another quantity of highly active bacteriophage (0,2 cc. to 10 cc. of liquid. The bacteriophage was still active in a dilution of  $10^{-10}$ ). Bacteriophage was superadded to demonstrate its influence still more conclusively than could be done with the bacteriophage already occurring in the Vlietwater.

The subjoined table shows the details of the experiment and gives a survey of the results achieved:

Contents of the tube.		Experiment begun	Lucid after how many times 24 hrs.
Filtered Vlietwater 5 cc + Flexner		23,9, '22	After $12 \times 24$ hrs all still turbid, after the next sojourn of $4 \times 24$ hrs $28^{\circ}$ C. all remain turbid.
" " " + Shiga Kruse		" "	
" " " + K. B. <sup>1)</sup>		" "	
" " " + Flexner + Bacteriophage 0,1		" "	
" " " + Shiga + Bact. 0,1		" "	
" " " + K. B. + Bact. 0,1		" "	$4 \times 24$ hrs lucid. $10 \times 24$ " " $6 \times 24$ " " $6 \times 24$ " " $9 \times 24$ " " $6 \times 24$ " "
Unfiltered Vlietwater 5 cc + Flexner		" "	
" " " + Shiga Kruse		" "	
" " " + K. B.		" "	
" " " + Flexner + 0,1 Bact.		" "	
" " " + Shiga + 0,1 Bact.		" "	
" " " + K. B. + 0,1 Bact.		" "	

The tests of the 2<sup>nd</sup> series were conducted as follows:

The fluid of two flasks, each holding 0,5 L. of bacteriophage-containing Vlietwater, was infected with such an amount of Flexner-culture as to render it quite turbid.

To the fluid of one of the flasks 20 mgms of KCN was added, after which the flask was well fitted with a rubber stopper. Both flasks were placed at room-temperature in diffuse daylight.

After a week the fluid of the flask without KCN had become quite clear, whereas the KCN-flask still contained a turbid fluid. In the former a large number of protozoa were found, which were lacking in the latter.

On the eleventh day of the experiment the KCN flask was also getting more lucid and protozoa were noticeable in it. After a fortnight the fluid in either flask was clear.

<sup>1)</sup> K. B. is a Flexnerstock resistant to any bacteriophage action.



The phenomenon exhibited in the KCN flask is to be interpreted by the fact that at the beginning of the experiment the KCN destroys the vegetative forms of the protozoa and consequently they are prevented from clearing away the germs present in the water. The cysts of the protozoa are not killed by KCN. After a week so much of the KCN has been decomposed through contingent chemical processes, that the cysts again grow into vegetative protozoa, which devour the Flexner bacilli, present in the water.

### CONCLUSIONS.

When summarizing our results it must be concluded that the significance of the bacteriophage for the self-purification of water is no doubt only small. I for one did not succeed in establishing the slightest influence.

The purification is effected in the absence of the bacteriophage, whereas its presence does not accelerate the process, nor render it more complete.

The experiments again yield conclusive evidence for the prominent rôle played by protozoa in the self-purification of water.

When, under such circumstances as the laboratory enables us to establish, we eliminate the protozoa, the self-purification of water is entirely arrested even though bacteriophage be added to the water.

*(From the Laboratory for Tropical Hygiene of the  
Leyden-University).*

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